U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-257 182

Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, II (December 1975, Hollywood, Florida)

Research Triangle Inst.

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

Jun 76

257106

PB 257 182

[illegible]

[illegible]

Environmental Protection Technology Series

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-76-149	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, II (December 1975, Hollywood, Florida)		5. REPORT DATE June 1976 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Franklin A. Ayer (Compiler)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P.O. Box 12194 Research Triangle Park, North Carolina 27709		10. PROGRAM ELEMENT NO. EHB529 11. CONTRACT/GRANT NO. 68-02-1325, Task 57
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 2-4/76 14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES IERL-RTP Task Officer for this report is William J. Rhodes, Mail Drop 61, Ext 2851.

16. ABSTRACT

The report covers EPA's second symposium on the environmental aspects of fuel conversion technology. The symposium was conducted at the Diplomat Hotel, Hollywood, Florida, December 15-18, 1975. Its main objective was to review and discuss environmentally related information in the field of fuel conversion technology. Specific topics were environmental problem definition, process technology, control technology, and process measurements.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Process Variables	Air Pollution Control	13B	13H,07A
Fuels	Industrial Processes	Stationary Sources	21D	
Conversion	Control	Problem Definition		
Environmental Engineering	Measurement	Process Technology		14B
Environments		Control Technology	05E	
		Process Measurements		

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 389
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE 10.75

EPA Form 2220-1 (9-73)

*U.S. GOVERNMENT PRINTING OFFICE: 1976-641-317/5515 Region No. 4

PRICES SUBJECT TO CHANGE

EPA-600/2-76-149
June 1976

SYMPOSIUM PROCEEDINGS: ENVIRONMENTAL ASPECTS OF FUEL CONVERSION TECHNOLOGY, II

(DECEMBER 1975, HOLLYWOOD, FLORIDA)

Franklin A. Ayer (Compiler)

Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

Contract No. 68-02-1325, Task 57
Program Element No. EHB529

EPA Task Officer: William J. Rhodes

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

1a

FOREWORD

The proceedings for the symposium on "Environmental Aspects of Fuel Conversion Technology, II," is the final report submitted to the Industrial Environmental Research Laboratory for the Environmental Protection Agency Contract No. 68-02-1325. The symposium was held at the Diplomat Hotel, Hollywood, Florida, December 15-18, 1975.

The main objective of the symposium was to review and discuss environmentally related information on coal conversion technology. Papers were presented that covered a summarization of major environmental programs and contaminants in coal, process technology, control technology, process measurements, sampling and analytical information pertinent to coal gasification and liquefaction, and product usage.

Mr. William J. Rhodes, Chemical Engineer, Industrial Environmental Research Laboratory, Environmental Research Center, Environmental Protection Agency, Research Triangle Park, North Carolina, was the Project Officer and General Chairman of the Symposium.

Mr. Franklin A. Ayer, Manager, Technology and Resource Management Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, North Carolina, was the Symposium Coordinator and Compiler of the proceedings.

Table of Contents

(* indicates speaker)

Page

15 December 1975

Opening Comments 3
John K. Burchard, Ph.D.

Session I: ENVIRONMENTAL PROBLEM DEFINITION, PART A 5
Gary J. Foley, Ph.D., Session Chairman

EPA's Energy/Environmental Program 7
Stephen J. Gage, Ph.D.

The President's Synthetic Fuels Commercialization Program 17
Matthew J. Reilly, Ph.D.

Environmental Controls and Synthetic Fuels 21
S. B. Alpert

Federal Regulation of Atmospheric Emissions From Coal Gasification Plants 27
James F. Durham

Summary of Multimedia Standards 33
John G. Cleland

An Investigation of Trace Elements in Coal 39
H. J. Gluskoter, Ph.D.,*
R. A. Cahil,
W. G. Miller,
R. R. Ruch, and
N. F. Shimp

Geochemistry of Trace Elements in Coal 47
Peter Zubovic

Session II: PROCESS TECHNOLOGY 65
E. C. Cavanaugh, Session Chairman

Trace Elements and Major Component Balances Around the Synthane PDU Gasifier . . . 67
A. J. Forney,*
W. P. Haynes,
S. J. Gasior,
R. M. Kornosky,
C. E. Schmidt, and
A. G. Sharkey

Table of Contents (con.)

Page

CO_2 Acceptor Process 83
Carl Fink,
George Curran,* and
John Sudbury

Effluent Considerations in Coal Gasification 91
Frank C. Schora and
Donald K. Fleming*

Bigas Process 105
V. D. Kliewer* and
V. L. Brant

16 December 1975

Session II: PROCESS TECHNOLOGY (con.)
E. C. Cavanaugh, Session Chairman

The Winkler Process, A Route to Clean Fuel From Coal 117
I. N. Banchik

Pressurized, Stirred, Fixed-Bed Gasification 125
D. W. Gillmore, Ph.D.,* and
A. J. Liberatore

The Westinghouse Fluidized Bed Combined Cycle Process: Status of Technology and Environmental Considerations 133
L. A. Salvador,*
E. J. Vidt, and
J. D. Holmgren

Role of Gasifier Process Variables in Effluent and Product Gas Production in the Synthane Process 153
M. J. Massey, Ph.D.,*
D. V. Nakles,
A. J. Forney, and
W. P. Haynes

Environmental Aspects of Synthoil Process for Converting Coal to Liquid Fuels 179
Sayeed Akhtar, Ph.D.,
Sam Friedman, and
Paul M. Yavorsky
(Presented by James W. Mulvihill)

Environmental Aspects of the SRC Process 183
Russell E. Perrussel,*
Walter Hubis, and
J. L. Reavis

Table of Contents (con.)

Page

Coalcon Liquefaction
Edward T. Coles
(Paper presented by John Hall, but not submitted for publication)

Session III: CONTROL TECHNOLOGY 191
René R. Bertrand, Ph.D., Session Chairman

Low and Intermediate Btu Fuel Gas Cleanup 193
C. B. Colton,*
M. S. Dandavati, and
V. B. May

The Benfield Activated Hot Potassium Carbonate Process:
Commercial Experience Applicable to Fuel Conversion Technology 217
D. H. McCrea

Coal Conversion Process Wastewater Control 225
W. A. Parsons, Ph.D.,* and
R. A. Ashworth

17 December 1975

Session III: CONTROL TECHNOLOGY (con.)
René R. Bertrand, Ph.D., Session Chairman

A Tapered Fluidized-Bed Bioreactor for Treatment of Aqueous Effluents
From Coal Conversion Processes 233
Charles D. Scott, Ph.D.,*
Charles W. Hancher,
David W. Holladay, and
George B. Dinsmore

Climatic Effects on Wastewater Treatment 241
Stanley L. Klemetson, Ph.D.

Waste Management of Fuels Processing Effluents 253
G. W. Grove
(Presented by Ronald V. Trense)

Control Technology R&D Needs 259
C. E. Jahnig,*
R. R. Bertrand, Ph.D., and
E. M. Magee, Ph.D.

Table of Contents (con.)

Page

Session IV: PROCESS MEASUREMENTS 267
James A. Dorsey, Session Chairman

Measurement Programs for Environmental Assessment 269
R. M. Statnick, Ph.D.,* and
L. D. Johnson, Ph.D.

Sampling Procedures for Process Streams 275
C. A. Flegal, Ph.D.,* and
J. W. Hamersma

Analytical Techniques for Sample Characterization in Environmental Assessment Programs 285
C. H. Lochmüller, Ph.D.

Evaluation of Particulate Characterization Techniques 293
H. Mahar, Ph.D.,* and
N. Zimmerman, Ph.D.

18 December 1975

Session V ENVIRONMENTAL PROBLEM DEFINITION, PART B 305
Robert P. Hangebrauck, Session Chairman

Water Requirements for an Integrated SNG Plant and Mine Operation 307
D. J. Goldstein, Sc.D.,* and
R. F. Probstein

Sulfur Emission Controls for a Coal Gasification Plant 333
Milton R. Beychok

Low Energy Gas Retrofit to Industry 341
D. A. Ball

Combined-Cycle Power Systems 359
F. L. Robson, Ph.D.,
W. A. Blecher, and
A. J. Giramonti*

NO_x Considerations in Alternate Fuel Combustion 373
G. Blair Martin

Environmental Impact and R&D Needs in Coal Conversion 395
E. M. Magee, Ph.D.,*
R. R. Bertrand, Ph.D., and
C. E. Jahnig

15 December 1975

Opening Session

William J. Rhodes
General Chairman

OPENING COMMENTS

John K. Burchard, Ph.D.*

It is a real and sincere pleasure to welcome you to our second symposium on the Environmental Aspects of Fuel Conversion Technology. As I indicated at our first symposium in St. Louis in May of 1974, we really don't have any need to justify the importance of establishing a viable industry for the conversion of coal, liquid and gas, as fuels. With the cooperation of American industry and universities, the Federal Government has already initiated many programs with large amounts of funds to accelerate development of this technology. However, the establishment of this technology without the protection of the public's health and welfare would be a real mistake. It would brand our country as one which neither cares for all its citizens nor possesses the technical know-how all this would create.

Within the Federal Government, assessment of environmental problems relating to this technology is one of the primary responsibilities of the Environmental Protection Agency, and in particular our Industrial Environmental Research Laboratory. We are currently negotiating various contracts for the performance of studies aimed at finding solutions for these problems. Up to this time, our evaluations have necessarily been limited mostly to existing data and engineering estimates. However, our new studies will lead to the acquisition of new data that will be used to expand and update our environmental assessments. These data have to be acquired on a continuing basis in order for us to keep abreast of the technological changes that will emerge while progressing from bench scale through demonstrations in commercial status.

Why do we need this information? Primarily for assurance that a given potential problem is either insignificant or can be handled by existing technologies. Where there are problems, controls will have to be developed and applied. This can be done most efficiently by full cooperation on the part of all Federal agencies and their contractors as well as by other private and public organizations. Meetings such as this, we hope, can do much to stimulate the necessary cooperation and provide the opportunity for those involved to assure for themselves, as well as to assure each other, that their efforts are complementary rather than duplicative or opposing in nature. It should be obvious that the development of either conversion technology or environmental control technology, without proper consideration of the other, is both unacceptable and unworkable.

Fuel Conversion Technology in and of itself is sufficiently complex. The additional consideration of the environmental effects and control compounds that complexity, particularly as the effective control has a decidedly significant economic impact. EPA is concerned about both factors, control and cost. Our goal is to aid and achieve the most environmentally sound fuel conversion systems at the lowest possible overall cost. This concern not only means developing efficient add-on controls, but also investigating, developing and promoting the use of more efficient operating procedures and optimum processes. These efficiency improvements would include, for example, process modifications and the recovery and reuse of environmentally damaging constitutents that have economic value.

Because of a certain increase in coal utilization during the next few years, we just don't know when all environmental pollutants will be adequately identified and modified, or when the effect of all pollutants will be adequately measured. Obviously then, all control systems can not be defined precisely at this time or in the foreseeable future. However, in order to permit commercialization with minimum delay, existing controls must be applied to known problems; potential problems must be assessed; and controls for these potential problems must be evaluated, utilized, modified or developed as necessary and as soon as possible.

This symposium is expected to provide an exchange of meaningful information between process developers, process users and environmental groups. The first session provides information on various overall coal programs, potential pollutants in coal and possible environmental standards. Subsequent sessions present some of the processes and control technologies that are being considered. These are followed by a session dealing with the sampling analysis of process and effluent streams. The final session defines environmental problems in terms of today's information.

I think that the value of free and open meetings such as this is evident—not only because of the information to be exchanged during the meeting, but because of the stimulus it provides for continuing communications between participants and attendees long after the symposium adjourns. We in EPA, as well as in other Federal, local and State government organizations, are in

---

*Director, Industrial Environmental Research Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina.

Proceding page blank

business to serve you and the rest of our country. In order to do the most effective job, we all need the most valid information available when making decisions. Much of this information can come from this group. The better the information, the better will be the decision for all concerned.

In conclusion, I hope you will enjoy your stay here and get something meaningful and productive from this meeting. I hope further that you will become involved with each other's interests and activities both during and after the formal sessions. Again, I'd like to extend my most sincere welcome to all.

15 December 1975

Session I:

ENVIRONMENTAL PROBLEM DEFINITION, PART A

Gary J. Foley, Ph.D.
Session Chairman

EPA's ENERGY/ENVIRONMENTAL PROGRAM

Stephen J. Gage, Ph.D.*

It is a pleasure for me to be here this morning, Gary, and thank you for the very kind introduction. I am surprised that the three people who preceded me up here to the platform have not acknowledged the physical surroundings. I think this is a marvelous place for a symposium. I do not know how you manage to keep everyone sitting out here in the audience when there is all that beautiful weather outside and such a lovely location. I just wish I were going to be able to be here longer and we could run the meeting for about 2 or 3 weeks so we could really enjoy the surroundings. I also add my congratulations to the Synthetic Fuel Group at the Industrial Environmental Research Laboratory. It looks like a very excellent session they have arranged here and I am glad to be able to participate.

The 1973 Arab oil embargo brought home to Americans the realization that we would have to depend increasingly on our domestic energy resources. If fuels were to be extracted, transported, processed, converted, etc., as well as utilized, on American shores, then we reasoned that the American environment would receive all of the impact of increasing energy use.

Although the measures required during the Arab oil embargo to mitigate the impact of the oil cutoff were almost exclusively conservative—belt tightening is probably the most appropriate term—we recognized at that time that the problems of inadequate domestic energy supplies, inefficient use of those supplies, and the necessary environmental damage resulting from their development and use, would probably be with us for a good many years. If nothing else, the oil embargo served as that very useful "slap-in-the-face" that you see in the television commercial—"I think we needed that!" The only thing that disappoints me is that we have not awakened nearly as much as the television performers seem to awaken with their slap-in-the-face. At least we are not doing a great deal about it even if we have awakened.

At the Federal level, there has been a considerable expansion of research on both the energy technologies and the associated environmental research. The program and the capabilities within the environmental research are scattered among a variety of departments and agencies. This calls for and requires centralized coordination of these programs so that our national energy goals can be matched with an effective R&D program in that critical area where energy needs and environmental protection goals overlap.

Major Federal Government involvement in energy R&D goes back to the early 1950's with the major historical emphasis on nuclear power. The Federal R&D concentrated first on the lightwater nuclear reactor and, later, on the liquid metal fast breeder reactor. The first major comprehensive study of national energy R&D needs and the role of the Federal Government in meeting those needs was called for by President Kennedy in the early 1960's. That study concluded in the so-called "Cambel Report" that concluded we did not face insurmountable problems in energy or energy R&D. The Federal Government's role at that time was seen as a limited one. Of course the underlying assumptions in that study were based on the then widely prevalent view that we had nearly inexhaustible domestic oil and gas resources.

In 1967, President Johnson established an Energy Policy Office within the Office of Science and Technology to sponsor a thorough study of energy resources. The first general results of those studies were incorporated in President Nixon's first energy message to Congress in 1971. Energy/environmental R&D, which had long been languished as a "poor stepchild," was given its first major public visibility in that address.

As the danger signals became apparent in the Mideast during early 1973, Administration and Congressional consensus for increased Federal spending on energy R&D developed: In the summer of 1973, the President directed the Chairman of the Atomic Energy Commission to prepare a comprehensive and integrated national energy R&D plan. The result, entitled *The Nation's Energy Future* and commonly referred to as the *Dixie Lee Ray Report*, was released in December 1973. Drawing upon the efforts of 36 Federal departments and agencies, as well as the private sector, it recommended a 5-year, 10-billion-dollar energy R&D program to achieve national energy self-sufficiency through the development of five energy resource areas—energy conservation, oil and gas, coal, nuclear, and advanced energy systems.

The Ray Report helped shape the Federal budget requests for the fiscal year 1975. These requests contained a substantial increase in energy R&D, including an increase for the environmental aspects of the major thrusts in energy resource development. As you can see in table 1, the Administration, through EPA's budget, requested 191 million dollars in FY 1975 for the

---

*Deputy Assistant Administrator, Office of Energy, Minerals, and Industry, Environmental Protection Agency, Washington, D.C.

Preceding page blank

Table 1. Background

Early 1960's (Kennedy)	– First major comprehensive study of energy R&D needs. The "Cambel Report" concluded that the problems were not insurmountable since we had nearly inexhaustible domestic oil and gas resources!
1967 (Johnson)	– Energy policy office established to "sponsor a thorough study of energy resources"
1971 (Nixon)	– First general results of study, referred to above, incorporated into the President's first energy message to Congress
1973 (Nixon)	– "The Nation's Energy Future" (The Dixie Lee Ray Report) prepared and released. Recommendation: A 5-year $10 billion energy research and development program
1974	– FY 75 Federal budget request of $191 million. $134 million authorized by Congress of which about $50 million was for the interagency program
1974	– Two interagency task forces established by OMB: • Health and environmental effects of energy use • Environmental control technology for energy systems
Late 1974	– Task force reports issued - identified program gaps and located target areas for "pass through" funds

energy/environmental R&D program. The Congress authorized 134 million dollars late in 1974. The interagency portion of that program was about 40 percent of the total, approximately 50 million dollars.

Following the release of the Ray Report and initial formulation of the 1975 budget by OMB, two interagency task forces were established by OMB and the Council on Environmental Quality to examine ongoing Federal research programs and to recommend allocations of funds which would provide the most effective integrated environmental/energy R&D program. Their reports covered two areas—health and environmental effects of energy use and environmental control technology for energy systems. Issued in November 1974, the task force reports were developed by key representatives from more than a dozen Federal agencies, departments, and laboratories, all involved in energy-related environmental research. One of the major purposes of the reports was to determine whether serious gaps existed in the overall Federal energy/environmental R&D program. By performing a crosscut review of the entire program, it was possible to identify such gaps, to determine areas where adequate support was available for national energy goals, and to locate target areas for supplemental EPA "pass through" funds. Thus, EPA, in implementing the interagency program based on the two task force reports, was in an excellent position to help maintain a balanced and coordinated Federal energy/environmental R&D program.

Also late in 1974 came the establishment of the Energy Research and Development Administration (ERDA) through enabling legislation. The establishment of ERDA created the centralized location within the Federal government for the development of energy technology. It also supported a major program of environmental research which had been taken over from the Atomic Energy Commission. As we move ahead toward the development of the new energy technologies, the role of ERDA will undoubtedly increase. It will, I believe, probably be concentrated on the environmental research that is required to make sure that those energy technologies do not degrade the environment.

Overall planning and coordination of the Federal interagency energy/environmental R&D effort, conducted under EPA auspices, is the responsibility of the newly created Office of Energy, Minerals, and Industries within EPA's Office of Research and Development (ORD). The Office of Energy, Minerals, and Industry (figure 1) is one of four major headquarters offices within ORD. Each of those headquarters offices has associated with it two or more of the 15 EPA field laboratories specializing in various areas of environmental research and development.

Within the Office of Energy, Minerals, and Industry, there are two major divisions: one is the Industrial and Extractive Processes Division which concentrates on multimedia, long-range planning, and coordination in the area of industrial and mineral processes; and the other, the Energy Processes Division, has responsibility along the same lines as they relate to energy activities.

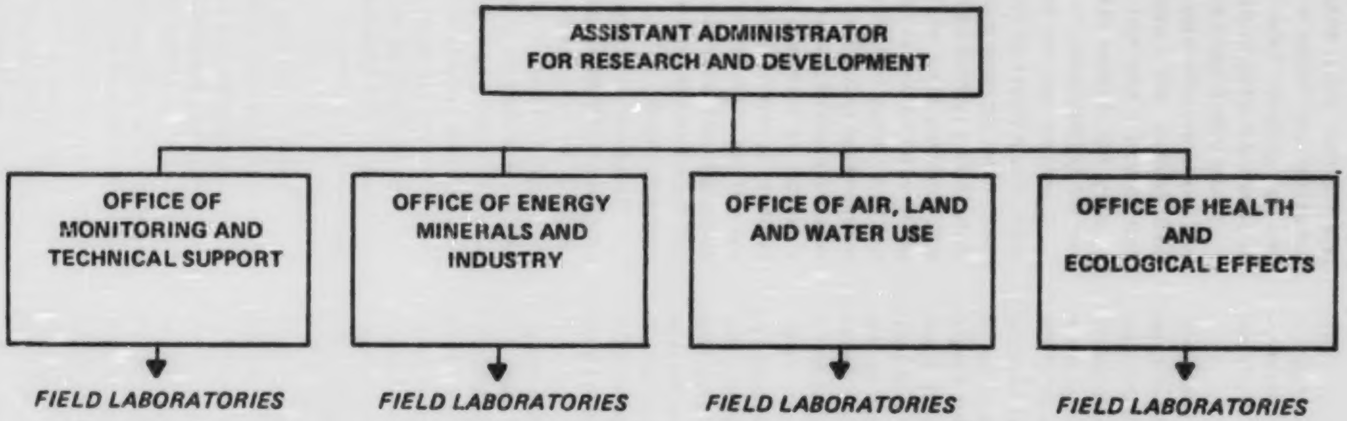

ASSISTANT ADMINISTRATOR FOR RESEARCH AND DEVELOPMENT
OFFICE OF MONITORING AND TECHNICAL SUPPORT
OFFICE OF ENERGY MINERALS AND INDUSTRY
OFFICE OF AIR, LAND AND WATER USE
OFFICE OF HEALTH AND ECOLOGICAL EFFECTS
FIELD LABORATORIES
FIELD LABORATORIES
FIELD LABORATORIES
FIELD LABORATORIES

Figure 1. EPA Office of Research and Development Headquarters Organization.

In addition, there is an Energy Coordination Staff. This staff has the responsibility of coordinating the health and environmental effects part of the interagency program both within the Environmental Protection Agency as well as with other Federal agencies.

For planning purposes, the control technology development program has been divided into five program areas as shown in figure 2. The Integrated Technology Assessment Program area is implemented and coordinated by the headquarters staff because of its key role in assuring the utility of research results from all of the program areas. EPA's two Industrial Environmental Research Laboratories, which report to the Office of Energy, Minerals, and Industry, and six other Federal agencies, are responsible for carrying out the other program areas. Since the Fuel Processing area is of most interest to this audience, I will restrict myself to that area. The fuel processing area is promoting and participating in the development of advanced technologies for fuel processing by providing environmental control technology development and characterizing environmental emissions and effluents. It is especially important that these efforts support the needed information flow between the energy technology developers and the regulatory offices to insure that standards do not delay or prevent energy development, yet establish adequate regulations to protect the nation's environmental quality.

In fiscal year 1975, as I mentioned, the energy/environmental R&D program was appropriated 134 million dollars of which approximately 21 million was allocated to the Fuel Processing area. In fiscal year 1976, the funding appropriated for the entire program is 100 million and, assuming that the overall budget will remain at approximately 100 million dollars per year through fiscal year 1980, funding for the Fuel Processing program is projected to increase as shown in figure 3. Here you see the allocation between the subprograms within Fuel Processing and the projected growth in the synthetic fuel area, which we feel is necessary in order to complement the efforts in the Energy Research and Development Administration and in the private sector.

I should interject a note of uncertainty at this particular time with which you are probably quite familiar; that is, the Conference report of the ERDA authorization bill was defeated in the House last Thursday. This raised some severe questions about how fast synthetic fuels will be developed in this country. I feel quite confident that some incentive program will probably emerge from this session of Congress; but it is almost anyone's guess, at this point, what the size of that incentive program will be and what will be the ultimate thrust.

Depending on the final disposition of this incentive program, how many dollars, how fast, and whatever stipulations are written in the appropriation, we may have to reprogram dollars within our budget or seek supplemental funding to provide EPA support.

I have tried to put the EPA synthetic fuel program into perspective with respect to the Federal Interagency R&D Program, and I would like to summarize in the final minutes I have here some of the results of the synthetic fuel program that EPA has been conducting over the past few years.

I am sure you will be hearing more about these results during the rest of the symposium. As you can see, much effort has gone into analyzing coals which are likely to be converted into synthetic fuel. This is probably providing some of the best information on the geochemistry of the coal and should be of considerable benefit to energy technology development as well as to environmental protection. Engineering studies to determine the potential pollutant releases have been made on a number of processes, as can be seen in table 2: Synthoil, Synthane, Lurgi, etc. This table also shows some of the results of the control technology studies, particularly on high-temperature, high-pressure processes and the efforts directed at first generation coal conversion technologies.

The Office of Energy, Minerals, and Industry has established some very rigorous objectives for itself over the next few years. These are in response not only to internal planning, but in response to the reality that we all face—that everyone is going to have to do a super job in order to make sure that the fine rhetoric we have evolved about bringing environmental and energy goals together in this emerging area comes to pass. This is a very, very tough challenge. In the environmental assessment area, the five objectives shown in table 3 have been given very high priority by the Office of Energy, Minerals, and Industry. If, in the future, legislation is passed through Congress to provide incentives to the synthetic fuels industry, these five objectives will assume a very high priority because it will be on the basis of the words referred to in table 2 that the next generation of air and water standards will have to be established. I will refer just briefly to the objectives of the control technology development program (table 4). As you are well aware, most of the control technology work will be carried out as part of the energy systems development.

There will be generic types of control technology needs which are closely related to control technology work being done in other areas by the Industrial Environmental Research Laboratory at the Research Triangle Park. I think that technology transfer from some of these areas to the synthetic fuels area can be very valuable. The magnitude of these efforts will depend both on the results of the environmental assessment program

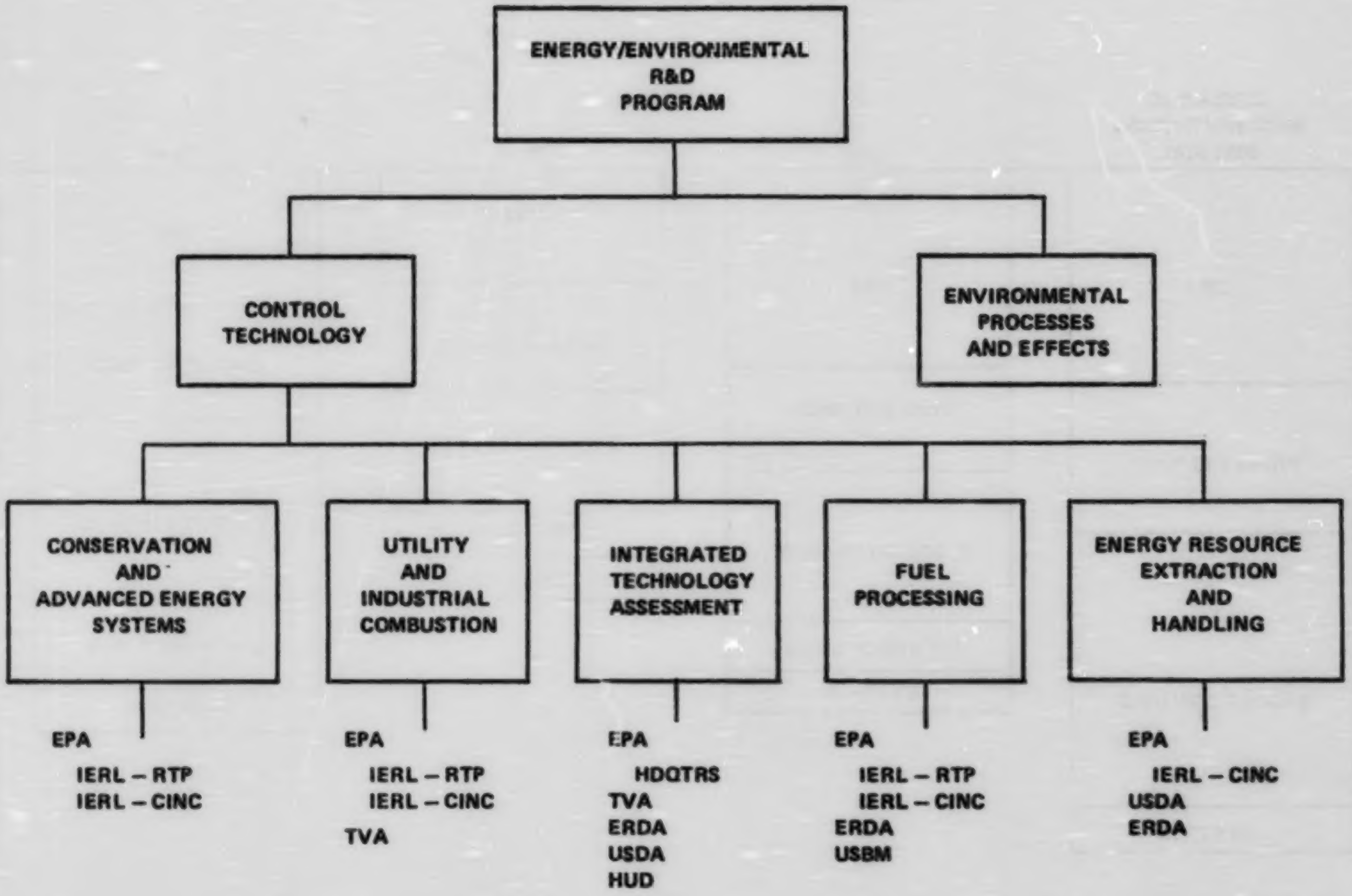

ENERGY/ENVIRONMENTAL R&D PROGRAM
CONTROL TECHNOLOGY
ENVIRONMENTAL PROCESSES AND EFFECTS
CONSERVATION AND ADVANCED ENERGY SYSTEMS
UTILITY AND INDUSTRIAL COMBUSTION
INTEGRATED TECHNOLOGY ASSESSMENT
FUEL PROCESSING
ENERGY RESOURCE EXTRACTION AND HANDLING
EPA
IERL – RTP
IERL – CINC
EPA
IERL – RTP
IERL – CINC
TVA
EPA
HDQTRS
TVA
ERDA
USDA
HUD
EPA
IERL – RTP
IERL – CINC
ERDA
USBM
EPA
IERL – CINC
USDA
ERDA

Figure 2. Energy/environmental R&D program.

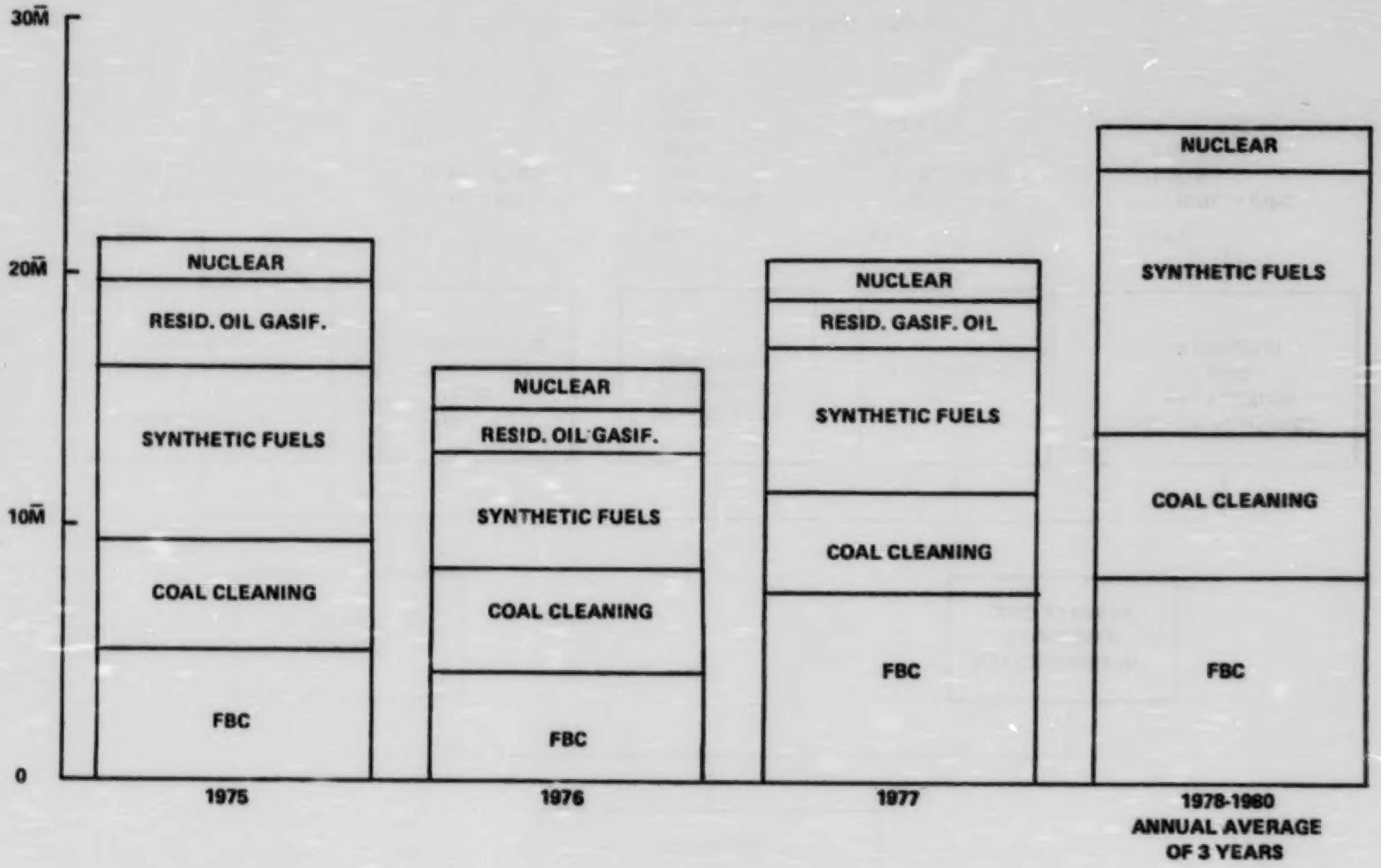


Figure 3. Funding summary for fuel processing program.

Table 2. Results of synthetic fuels program to date

- Analyzed over 1,500 coal samples from more than 100 eastern and midwestern coal sources and characterized them for pollution potential.
- Identified potential pollutant releases by seven conversion processes:
  - Koppers-Totzek gasification
  - Synthane gasification
  - Lurgi gasification
  - CO_2 acceptor gasification
  - Bigas gasification
  - COED liquefaction
  - SRC liquefaction
- Developed and demonstrated highly effective desulfurization process for high-temperature gas stream (at bench scale)
- Completed an analysis of high-temperature versus low-temperature cleanup of gas streams
- Completed an analysis of problems and opportunities in retrofitting industrial processes to utilize low-Btu gas
- Examined commercial-scale gasification plants in five foreign countries. Contracted for operational data and pollutant-emission measurement program on Lurgi units in several countries
- Sponsored a symposium in 1974 that produced a comprehensive report on the state-of-knowledge on environmental effects on fuel conversion processes
- Published a survey of potentially hazardous emissions from the extraction and processing of coal and oil

Table 3. Synthetic fuel program environmental assessment objectives

- Perform environmental testing of first generation coal conversion processes as negotiations permit.
  - Lurgi units in Yugoslavia, South Africa, and Poland
  - Fischer-Tropsch in South Africa
- Assess the effectiveness of available control technology for first generation coal conversion processes and prepare standards of practice manuals for environmental control.
- Perform environmental testing of second generation coal conversion processes being developed by ERDA.
  - Hygas, Institute of Gas Technology, Chicago, Illinois
  - Solvent refined coal, Pittsburgh and Midway, Fort Lewis, Washington
  - CO_2 acceptor, consol, Rapid City, South Dakota
  - Synthane, ERDA, Bruceton, Pennsylvania
- Determine requirements for control technology development for second generation systems.
- Review proposed environmental standards from the R&D viewpoint.

Table 4. Synthetic fuel program control technology development objectives

- Evaluate, develop, and/or demonstrate, as needed, best practicable control technology for:
  - Fuel storage, handling, and preparation
  - Raw product purification
  - Product and byproduct utilization
  - Waste treatment and disposal
- Provide environmental support and guidance on control technology development to ERDA and the industrial sector in their coal conversion R&D

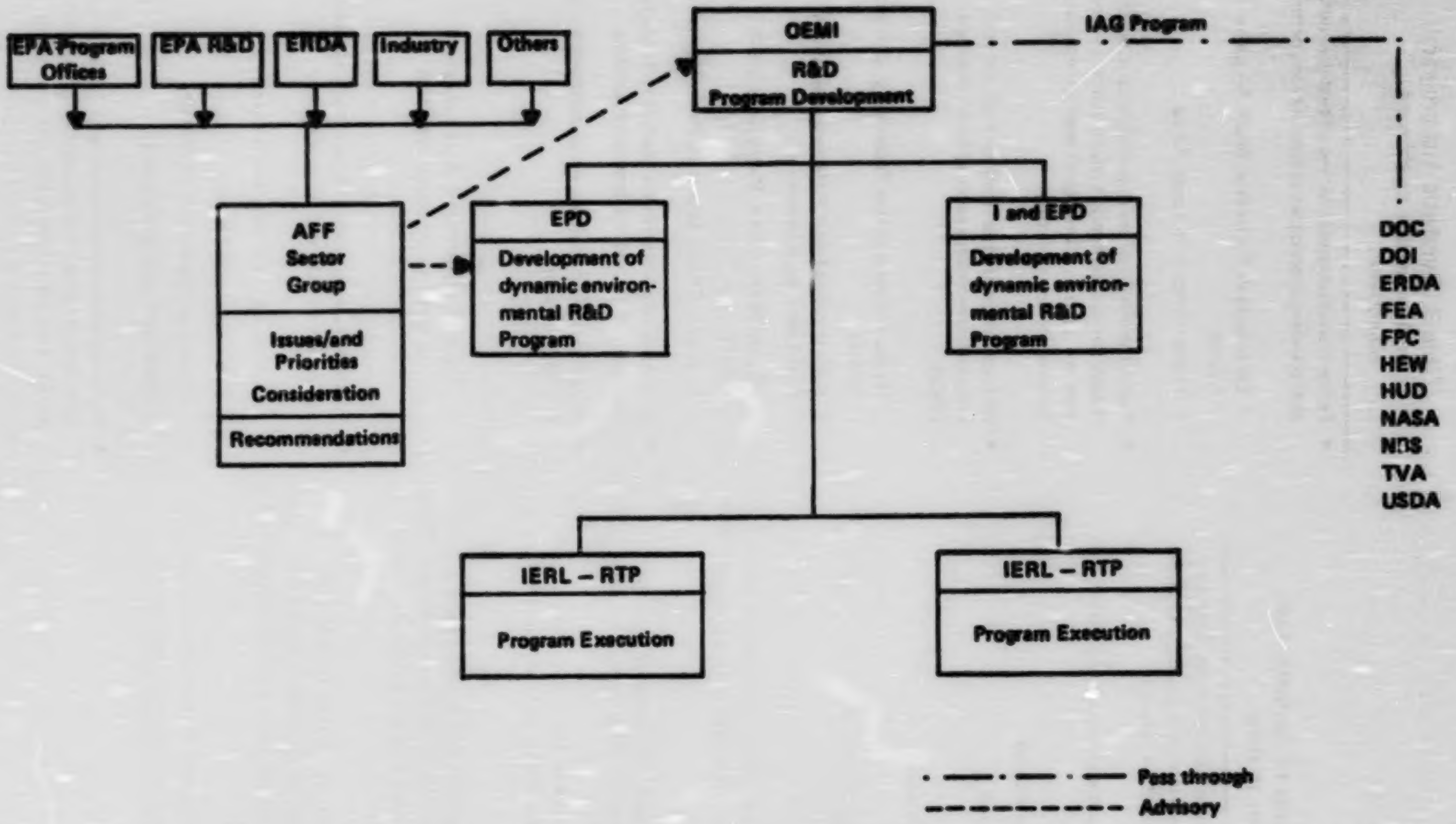

EPA Program Offices
EPA R&D
ERDA
Industry
Others
AFF Sector Group
Issues/and Priorities Consideration
Recommendations
OEMI
R&D Program Development
IAG Program
DOC
DOI
ERDA
FEA
FPC
HEW
HUD
NASA
NBS
TVA
USDA
EPD
Development of dynamic environmental R&D Program
I and EPD
Development of dynamic environmental R&D Program
IERL – RTP
Program Execution
IERL – RTP
Program Execution
Pass through
Advisory

Figure 4. Advanced fossil sector group relationship.

referred to in table 3 and on the relative magnitude of efforts by ERDA and private industry to provide the advanced control technology.

Before closing, there is one final activity in my office that I would like to mention. In order to promote communication and insure EPA's R&D program obtains advice from the best sources, I have formed three sector groups. One of these—the Advanced Fossil Fuels Sector Group, which is chaired by Dr. Gary Foley—has the responsibility for the synthetic fuel program. On figure 4 you can see the relationships between the sector groups, which is shown in the center left, and the rest of the office structure. The purpose is to bring together all of those people in the energy development area—environmental control technology development, environmental effects studies, regulatory efforts, and industrial activities. The membership of the sector groups is shown in table 5 and, as you can see, there is a very wide representation from the various interest groups. The sector groups are overseen by an executive committee which plans the agenda for a meeting, summarizes the meeting results and recommendations, and provides the recommendations to the Office of Energy, Minerals, and Industry for incorporation as appropriate in the planning of our future research and development programs. To date, we have had two successful meetings of the group within the past 6 months, and we look forward to many future successes.

That concludes my presentation this morning. I wish you very well in this session and hope that this serves as the point at which we really take off to do the hard-nosed environmental assessment and control technology development which we are going to have to do. We have done a great deal of talking over the last couple of years, and now we have to really begin with the important work that is at hand. I look forward to having many of you represented in this room work with us and with the other Federal agencies in making sure that all of our fine rhetoric is not just so many hollow words. Thank you very much.

Table 5. Advanced fossil fuel sector group meeting composition.

- Executive Board - EPA representatives (responsible for agenda)
- Sector group membership
  - Government
    - EPA (R&D, program offices, regions)
    - ERDA (environment and safety, fossil energy)
    - DOI (USGS, USBM)
    - FEA
    - NIOSH-HEW
    - DOD (Navy)
    - TVA
  - Industry and research groups
    - Consultants from:
      - American Petroleum Institute
      - Coal industry
      - Gas industry
      - Electric Power Research Institute
      - EPA R&D contractors

THE PRESIDENT'S SYNTHETIC FUELS COMMERCIALIZATION PROGRAM

Matthew J. Reilly*

Let me talk a little bit about the background to this paper. This is an effort that began in January 1975. It was initiated by the President's State of the Union message in which he referred to the need to both develop new technology for synthetic fuel, but at the same time see what needed to be done to remove some of the barriers and some of the constraints toward the intrastructure to the environmental, social, economic, institutional, refinement, regulatory, mining, and transportation aspect of synthetic fuels commercialization. And so, the President has directed that an interagency task force be formed with the objectives of seeing what could be done to use existing technology and encourage the private sector through a program of consensus, to build and operate first off accounting commercial skills into a plant, emphasizing domestic resources, coal, oil shale, and solid waste.

Now, a variety of financial incentives was mentioned by the President in his message, including low price guarantees and direct grants. And, incidentally, the Congressional action on Thursday was one in which they took exception—at least the House took exception—with the loan guarantee portion of this program. ERDA has existing authority to implement the other aspects of the program, and while the House's view was a disappointment, by no means does that mean the program is dead.

The output of this interagency task force was a two-phase program recommendation. Alternately aiming at a million barrels per day, but with a first phase target of 350 thousand barrels of synthetic fuel equivalent before 1985, it was viewed that this two-phase effort would provide information that would allow one to determine the best way to structure the second phase, and to do this with minimum environmental and other risks.

Now, I am going to talk principally about the environmental assessment, their other aspects of this program, and I can refer you to the task force's four-volume report which will be coming out the end of this month. The last volume to go to the printers was "Environmental Assessment" which is in the hands of the printers now. As soon as we get that volume back—and it runs about 1,000 pages—all four volumes will be released to the public as well as sent to the Council on Environmental Quality and other Federal agencies. The other volumes deal with an overview of the program with an analysis of its costs and benefits and a discussion of the various incentives that were considered and their breakdown and cost over time. Volume 4 deals with the environmental assessment.

We begin by looking at five coal regions and the principal oil shale regions that were viewed as being those parts of the country most likely to receive significant development within the time period. We selected illustrative synthetic fuel technologies emphasizing those that were believed to be commercially available today, but also looking at some second-generation technologies that were coming down the pike. We selected the uniformed size (roughly equivalent to 250 million cubic feet per day) by Btu gasification plant and analyzed the impact from units in fuel plants in each part of the country, using various types of coal and other regional differences. Then we looked at the impact from the conjunctive development such as mining, transportation, community expansion, water supply development, and so forth. This allowed us to assess what the impact of a single central plant of these various types would be in each of the geographical regions analyzed. In order to get a handle on the total aggregate impact of the program, we examined some alternative ways in which a million-barrels-per-day syn-fuel industry might be composed. We looked at several different production levels, 350 thousand barrels per day, one million, and 1.7. The impacts for each of these alternative industry compositions aggregated essentially as a matter of multiplying together as a first order of approximation the impact of a single plant by the number of plants that would go in each part of the country. After looking at the unavoidable impact of the resource commitments, alternatives to the syn-fuel program were analyzed; these are covered in detail in the Environmental Impact Statement. And finally, a unique aspect of this effort was the design then in the program of an environmental protection strategy to reduce and litigate the environmental effects. I will talk more about this strategy later.

Let us consider the five regions by coal-producing regions and the oil shale region that were analyzed. Appalachian and Eastern interior offering principally a high sulfur bituminous coal for union offering, lignite out of rivers for a subbituminous coal, and so on. We looked at the plans in terms of their size and the energy

---

*Dr. Reilly is acting Assistant Director for Environment and Safety, ERDA, Washington, D.C.

Preceding page blank

value, for all of the coal and oil shale answers are substantially the same and bring only about 10 percent. The biodegradable synthetic fuel from urban waste is smaller and it strives to function according to the amount of solid waste that would be available from a typical community of about 100 to 400 thousand population. Now I will not go into the details of analyzing the impact from a single plant. I think you can pretty well understand the methodology to be followed. For example, knowing what went into the plant in the way of coal, sulfur content, etc., we could compute what the emissions would be and then, doing some air quality modeling, we could determine whether the Federal air quality standards would be satisfied for the major pollutant. In this case, and under several atmospheric conditions, we satisfied ourselves that a Fisher truck plant located in the Appalachian region would, in fact, satisfy the three-R sulfur oxide concentration. This type of calculation was repeated then for all of the air pollutants and in the water area as well. We also looked at the socioeconomic impact, where we examined the buildup of the work force of the time in the construction phase and in the operational phase. For a high-Btu gasification plant, the number of employees would peak at about 3,000 during the construction phase and then level off to a steady state of about 800 employees during operation. Based upon the number of employees in using various socioeconomic multipliers, you could then determine the number of police cars, hospital beds, family secondary industries, etc., that would be required in the vicinity of the plant.

Having thus determined what the impact of a single plant would be, we looked at three different ways in which the industry might be composed, reflecting three different emphases on the fuel track. A pipeline gas emphasis with a high-Btu gas product, roughly half of the million-barrels-per-day would be high-Btu gas. Now since the goal of the programs proceeds to be of informational nature, all of these emphases contain a mix of all the different types of syn-fuel plants; so even in a high-Btu emphasis, in one we have a syn-crude from coal, syn-crude in oil shale, etc., included in the million barrels per day.

The two other emphases we examined were an industrial utility low Btu-fuel emphasis and a premium-liquid emphasis in which the syn-fuel production would be larger.

We note that the water requirements in terms of gallons per year are greatest in the Eastern interior and in the Appalachian region in all of the cases. This reflects in part the fact that the plant would be designed differently in the Eastern and Western regions of the country.

Some of the key findings for water quality were concluded based upon also examining the availability of water—would water be abundant in the Appalachian and Eastern interior regions for the million barrels per day industry. Sufficient water would also be available in the Powder River and Fork Union region and in the four corners of oil shale regions, but diversion from its present use as two-cent fuel would present various problems, and these are discussed in more detail in the statement.

We examined various impacts of the mining activities from downwater in quality as well as the effect of removing water from the streams and thus reducing the flow of those streams.

We find it noteworthy that the principle source of emissions would be the boilers and other process heat equipment, rather than the actual reactors and pieces of process equipment itself. For the most part, air quality standards can be met or somewhat constrained and one would not be able to locate the essential plants near major existing pollution forces or in locations with severe air quality standards. The matter of carcinogens received extensive treatment in the statement. This is one that limited experience, as this case indicates, is an industrial occupational health concern—the one that, with prudent occupational health measures, can be controlled. Our environmental protection strategy, to which I referred previously, calls for a comprehensive monitoring program to insure that this problem does not get out of hand. With respect to mining, we will ask by the findings here, particulates of nitrogen oxides represent the main pollutant, but we received no significant area-wide impact resulting.

Now about the resource requirements, I think the note-worthy point is that in all cases, over the 20-year life of a one-million-barrel-per-day syn-fuel industry with all of the three different cases at which we looked, the maximum drawdown of the available resources would be less than 3 percent in any region of the country. The finding here surprises us if there are adequate domestic resources available to support an industry. We point to the loss of water resources due to the damaging of aquifers during the mining activity; the possible loss of agricultural value in the land due to the mining activity; the loss from scenic resources, and the fact that here in terms of the land area affected, it is the community expansion and the conjunctive development that will, in fact, require more land area than the mining of the plant. And insofar as the community expansion is directly associated with people, and these people are going to need to be housed and provided services in any event, it is somewhat uncertain the extent to which that is a direct result of this program. There are some key findings with regard to the biological environment: the habitat disturbance leading to new climax communities even after the land has been restored; the revegetation and reclamation problems that are good fault in the semiarid areas of the West; the fact that moving into some of the remote areas and opening them up to increased population would also take the stress on some of those animal species that are least able to tolerate the proximities of man; and the impairment of the habitat due to the impact on waterfell being stream flow.

With respect to the increase in regional population, a key increment of the socioeconomic impact, we note the increase in the regional population as a percent due to the one-million-barrel-per-day industry.

It is to be seen that the oil shale region presents the largest population increase, approximately 55 percent over the present population in the areas. This would take place over the entire tenure or lifetime of the program leading to an average increase of 6 percent per year. That figure would be a manageable one if it were distributed evenly in this region. If it were not, that potential problem would then be impacted upon the environmental protection strategy that I will present shortly.

Other key findings in this socioeconomic area are in addition to the problems of large and rapid population increases. The changes in community lifestyles, the increased demands upon community services, and facilities there are beneficial impacts. Economic stimulus to the community would result, and there would be an increase in the tax base of new job opportunities. Finally, we note that the development will cause a permanent change in the remote areas from rural lifestyles into an urbanized industrial one. The environmental protection strategy then brought into the program is the direct result of the environmental assessments which were formed, and at this point let me digress. We began the environmental analysis at the same time that the other task forces were looking to the cost and the technology—the environment was not a weak sister that came in at the tail end of everything and an after-the-fact justification—what was it that one sought to do.

It was integral coming in at the very beginning and as a result inherent to the program design of some of these key elements—for essentially, the Environmental Advisory Board would represent the regions that would be affected, would represent the technical and scientific community, and would represent various government agencies including the Energy Research and Development Administration.

Environmental criteria would be essential in the proposal evaluation process. There are procedures developed and will be published in the *Federal Register* for State, local, and public involvement in the program like specific development plans. Environmental impact statements will accompany each major action under this program. Federal approval of the site developments would be a prerequisite to proceeding with the construction phase. Public hearings and opportunities for comments would be provided. The regional impact assistance is in the form of guaranteed loans to the impacted local communities, so that in the event that a facility would fail, the local community would not be left holding the bag for its front-end investment in intrastructure costs. I refer to the environmental monitoring program, the strict enforcement of the environmental standards.

Finally, the impact statement when it has identified some of the uncertainties at the same time identifies the type of research that would be needed to resolve those uncertainties.

There are some key areas here for environmental research. First, the effluent from fuel sites Commercial Processes Program would need to receive careful attention in our data-gathering activities. The essential program would include within it research on improved control technology on the effect of the pollution waste management technique for disposal of the solid waste, particularly, resulting from the oil shale processes and citing criteria needed to be a part, if you like, of the handbook which could accompany these technologies when they are presented to the Nation as commercially feasible.

Second, the intrastructural requirements—how one in fact does go about providing for community expansion when placed under the stresses of rapid population growth and do this in a prudent and economical fashion.

Third, optimum water usage. Until we actually put the best engineering talents to work in designing these full-scale commercial plants, we do not really know what might be the best we can do in the way of conserving water. This program will bring it forth.

Fourth, utility planning. Regular budgetation and reclamation are two other areas in which there are research opportunities in this program.

Well, that concludes my presentation. Again let me mention that the details of this environmental assessment are contained in our draft environmental impact statement which is at the printers now. I would hope that we can deliver it as a Christmas present to CQ. Thank you.

ENVIRONMENTAL CONTROL AND SYNTHETIC FUELS

S. B. Alpert*

The Electric Power Research Institute (EPRI) is the central research agency of the electricity industry. The organization has been in full operation for over two years and has launched a major program in coal conversion and utilization that has as one of its major objectives the economic utilization of the U.S. coal supply to provide fuel for electricity manufacture in an environmentally acceptable manner.

Since we are meeting in Florida, we must use the local football fever related to the upcoming Super Bowl game to draw an analogy to the status of synthetic fuels and the upcoming papers in this session. The process technology game is such that we are more or less just starting. The team is assembled on the 20-yard line having just received the kick-off. We have a game plan, and the ball has been snapped to our quarterback. He throws a pass down the field. As the receiver heads down field, a guy runs alongside writing rules that may or may not declare the play as legal. That is the role of the State and Federal EPA. In addition, as he turns to catch the ball, he is being kicked in the shin. That represents the environmentalist. Besides all this, and to perhaps push the analogy a bit too far, at the end of the field the goal posts are being moved from the 100-yard line and we are not really sure where the goal line will be set up. That represents the inflationary pressures that have escalated the cost of synthetic fuel development from what were considered $200 million problems, to what now are apparently $1 billion investments that are required to develop and demonstrate commercial power systems that utilize coal gasification of coal liquefaction. The risks with respect to private investment are rather large, and it is doubtful that any rational industrial management will have a reason for assuming such complex tasks without substantial Federal support.

Table 1 shows the 1976 budget of the Fossil Fuel Department. The electricity industry is prepared to pay for support of the research and development necessary to develop synthetic fuels. We anticipate that in future years, our expenditures will increase and we will have a substantial role to play in carrying out a directed program in cooperation with industry and the Energy Research and Development Administration (ERDA). The Fossil Fuel Department budget is a significant part of the overall Institute budget of about $130 million in 1976.

Table 2 shows the capacity of typical commercial plants that daily handle many thousands of tons of solids and liquids to produce the products required by our industrial society. The engineer has learned to take advantage of continuous processing systems that have reduced the costs of products to the public. None of the process technologies that are competitive alternates to current methods of supplying fuel for electricity generation has achieved such a status wherein it can be applied at such scales. We still have a great deal to learn before such plants can be confidentally designed and operated with components engineered for the service.

Table 1. Fossil Fuel Department Proposed 1976 Research and Development Plan Department Summary

Program	Funding Level ($\$10^6$)
Gasification	12.0
Liquefaction	10.9
Direct Utilization	3.7
Environmental Control & Combustion	12.2
Supporting Research	1.7
TOTAL	40.5

Table 2. Size of U.S. Industrial Plants in Tons/Day

Coal Fired Power Stations	12,000
Oil Refineries	50,000
Cement Plants	8,000
Ethylene Plants	2,000
Ammonia Plants	2,000

---

*The author is with the Electric Power Research Institute, Palo Alto, California.

Preceding page blank

A major area being supported by EPRI is the research and development required to convert coals to clean liquid fuels. Such products range from solid fuels cleaned of mineral matter and reduced in sulfur content to highly refined clean liquids that represent turbine fuels very much the same as fuels that derive from petroleum. Our program is relatively broad, but our major emphasis is in support of:

- Solvent Refined Coal
- H-Coal
- Exxon Donor Solvent

We believe that the three approaches should be pursued. Solvent Refined Coal (SRC) is a process technology that results in a clean solid boiler fuel. EPRI supports a 6 ton/day pilot plant in Wilsonville, Alabama in association with Southern Services, Inc. Over the last two years, successful operation of that facility has indicated that the process can be operated on selected U.S. coals to produce products to specifications set by the EPA. The noncatalytic SRC process technology is also being explored at Tacoma, Washington in a 50 ton/day pilot plant. Our SRC program is being coordinated with the federal sponsors of the Tacoma plant. Currently, cost estimates and plant designs are underway for large sized plants.

It is likely that this technology is ready for demonstration at the 1000 ton/day scale although some further development is still required that promises lower costs. Before much too long this process should be proved out in larger equipment. A number of utilities find the SRC fuel attractive for their systems.

The H-Coal process which represents direct catalytic coal liquefaction has been under development for a decade. This technology is one that has been too long at a small scale in the laboratory. EPRI has joined with other organizations and ERDA to prove out the process in a large pilot plant that will handle 250-600 tons/day of coal.

Recently our Board of Directors approved participation in the Exxon Donor Solvent technology. A test in large pilot plant equipment is scheduled for the late 1970's.

We believe that these three technologies represent process technology that is furthest advanced and that have strong teams able to complete the required development work.

Table 3 summarizes the pilot plants liquefying coal. When one realizes that about 40,000 barrels a day are required to fuel a single 1000 MW power station, one can see how far we still have to go before coal liquefaction can be considered a reality by the power industry. There are viable technologies, able teams, and established organizations with excellent capabilities. The major missing ingredient is the money to carry out the required program.

The gasification of coal was practiced in this country primarily to produce gaseous fuel in historic fuel gas producers, for illuminating gas and low-heating value fuel gas for domestic use. That industry all but disappeared after the second world war when low cost natural gas transmitted to population centers priced gaseous fuel from coal from the market.

An option that is of interest to the power industry is the utilization of gaseous fuel from coal in combination with power generation equipment to produce electricity economically in plants that can satisfy all environmental requirements. At this time, there are no plants in the United States producing gaseous fuel from coal being used to generate electricity.

Fuel gas from coal has a number of potential markets in the power industry. These include:

- retrofit of gas-fired boilers that have been curtailed from their natural gas supply,
- fuel supply for new boilers that require clean gaseous fuel free of particulates and pollutants,
- fuel supply for applications which use gas turbines and steam turbines combined for efficient utilization of energy, and
- generation of raw materials for
  - methanol production useful for peaking fuel,
  - hydrogen production,
  - reducing oxides of sulfur to elemental forms in advanced scrubber systems, and
- fuel supply for fuel cells.

The ideal gaseous component from coal for power generation is carbon monoxide. In contrast, the ideal gaseous component for the gas industry is methane. Thus, process technology of interest to the power industry that converts coal to gaseous fuel is a very different kind of system than that required to supplement natural gas supply. The emphasis in power systems is on process technology that can convert coal to gaseous fuel at a high capacity at modest pressure using relatively simple systems that have high reliability in conjunction with power generating equipment. A further requirement is that such systems be competitive with conventional pulverized fuel combustion with stack gas scrubbing. Taking account of the escalated price of crude oil and the likely shortage in the next ten to twenty years, the base loaded power station will tend to use nuclear power since those generating systems are high in capital cost and low in fuel cost. Thus, gasification plants will be used to satisfy what the power system engineer refers to

Table 3. Operating Pilot Plants Liquefying Coal
(Note: Excludes Bench Scale Units)

Process	Status	Capacity, Tons/Day	Source of Funds
Solvent Refined Coal	Operational	6-12	Southern Company EPRI
Solvent Refined Coal	Operational	50	ERDA
CONSOL CSF	Shut-Down	25	ERDA
H-Coal	Operational	3	ERDA, EPRI, Sun Oil, Amoco, ARCO, Ashland Oil Co.
Exxon EDS	Operational	1	Exxon
Gulf CCL	Construction	1	Gulf
Synthoil	Construction	8	ERDA, Bethlehem Steel

Note: EPRI = Electric Power Research Institute
ERDA = Energy Research and Development Agency

*Smaller scale units at various locations are investigating liquefaction alternates. Lummus, Universal Oil Products, and Continental Oil Co. as well as others have such efforts underway. In addition there are several coal liquefaction programs at the University of Utah, Auburn University, University of North Dakota, etc.

as intermediate load demand. Power systems that gasify coal to produce a fuel supply will therefore need to follow a demand curve that translates into a capability for starting up and shutting down under control.

Such power applications put a new requirement on the application of process technology that is very different from the conventional application of coal gasification technology for petrochemical applications, such as ammonia or methanol plants. There is considerable doubt that coal gasification plants can be "swung" to follow load demand of a power system.

Gasification using already existing technology that is represented by fixed bed, fluid bed, or entrained systems is uneconomic in competition with conventional power industry practice. The purpose of the EPRI program in gasification is to develop power systems that are:

- lower in capital cost,
- lower in net power cost,
- have high efficiency (Heat Rate), and
- lower in cooling water consumption.

In order to accomplish these objectives, a key technological need is the development of gas turbines of high reliability capable of operating in the range of inlet temperatures of 2500° F to 3000° F. Such a program of development is necessary to gain a large share of the power generation market. Currently available gas turbines operate at about 2000° F and are not considered of sufficient reliability.

Table 4 shows the gasifier characteristics that are ideally desirable which, when combined with efficient gas turbines, could produce a power generating system that has many desirable features.

Table 5 shows the key development issues that are being addressed in the program that is underway and being funded by Federal and industry sources. In this discussion we will not have sufficient time to deal in depth with each of these issues. In developing a system for power generation, all of these issues must be considered simultaneously for the particular gasification system under development.

Table 6 shows one of the reasons why this simultaneous consideration of these issues is needed. The last column shows the flame temperature of the gaseous fuel produced from a number of new systems. Note that the adiabatic flame temperature of some of the fuels is fairly low. There would be little reason to develop 3000° F gas turbines if the flame temperature is below the operating temperature of the gas turbine. The entire system must be considered in applying coal gasification for power industry applications.

Table 7 shows a number of the unresolved problems in developing power systems. These problems are common to all such systems and underline the need for development of power systems rather than gasifiers.

Table 4. Desirable Gasifier Characteristics

- Simplicity
- Easy Maintenance
- Minimum Number of Units and Stages
- Large Gasifier Capacity
- Minimum Coal Processing Upstream, Gas Cleaning
  - No Tars in Product Gas
  - Capability for Feeding a Caking Coal
  - Minimum Amount of Fine Dust
- Capability for Quick Shutdowns and Restarts
- Capability for Processing a Wide Variety of Coals
- No Gross Instabilities
- Capability for Load Following
- Capability for Operation at a Pressure Level Suited to the Integrated Combined-Cycle Installation

Table 5. Power From Gasification Combined Cycle Systems Key Development Issues

Integral Control

Load Following Capability

Turbine Reliability

Air Versus O_2 Gasification

Combustor Design

High Temperature Gas Turbine Development

Availability of Funds

System Reliability

Environmental Impact

Table 6. Low Btu Gas Characteristics

Gasifier	Clean-up System	Gas Temp. °F	Gas Pressure, Psia	Gas HHV Btu/Scf	Adiabatic Flame Temp. °F
Lurgi	Hot Pot	230	300	172	3350
BGC Slagger	Benfield	230	300	183	3600
C.E.	Stretford	105	16	105	2900
B & W	Stretford	105	65	84	2500
B & W	Benfield	230	65	68	2200
Foster Wheeler	Benfield	230	365	169	3600
Texaco	Benfield	230	350	79	2600

Table 8 summarizes an assessment of gasification technology. In order to resolve the fundamental question as to whether a gas turbine can be directly connected to a coal gasification system, a power system based on Lurgi technology is to be designed, constructed and operated by Commonwealth Edison Company. The system capacity is 25 MW and will utilize currently available gas turbines. It will also provide a test site for advanced gas turbines and an opportunity to study the control system required to permit following changes in electricity demand while using a number of U.S. coals having a range of caking properties.

Table 7

Effects of System Integration on Design, Interconnection and Operation of Each of the System Components:

- Influence of Gas Heating Value and Clean Up System on Combustor Design.
- Dual Fuel Capabilities and Gas Turbine Mismatch.
- Effects of Gas Quality Variations on Gas Turbine Operation.
- Gas Storage Requirements for System Buffering.
- Control of Multicomponent Integrated System.

Table 8. Coal Gasification Development Status

Currently Commercial

Lurgi – Fixed
Koppers-Totzek – Entrained
Winkler – Fluid
Atmospheric Producers – Fixed

Improved Processes of Near Term Potential (Pre- 1985)

British Gas Slagging – Fixed
Babcock & Wilcox – Entrained
Texaco – Entrained
Combustion Engineering – Entrained
Pressurized Koppers-Totzek – Entrained

Second Generation Processes (Post- 1985)

Foster Wheeler – Entrained
IGT Fluid Bed – Fluid
Westinghouse – Fluid
COGAS – Fluid
Conoco – Fluid
Union Carbide – Battelle – Fluid

Advanced Concepts

Atomics International – Molten Carbonate
Fast Fluidized Bed

The EPRI program also includes support of the British Gas Council slagging gasifier. This development, which is cofunded with 13 other organizations, is underway at Westfield, Scotland. It represents a significant advance over Lurgi technology which will not be gone into in detail. The slagging gasifier is in an advanced state of development and if steady progress is realized could represent an evolutionary step for a system generating power.

EPRI has also joined with ERDA and the Combustion Engineering Company in a pilot plant test of an atmospheric pressure two-stage entrained gasifier. This technology seems to represent a low-cost producer of gaseous fuel suitable for power generation.

The fossil fuel department also has programs in:

- direct utilization of coal, and
- environment and combustion.

These subjects are outside the interest of this conference and will not be discussed.

At this time, synthetic fuels from coal are at the pilot plant level. The power industry, through EPRI, has underway a program that will lead to power system options in the next decade that are economic. Environmental control of emissions from synthetic plants, while of importance, could represent a counter productive block in the development of new technology. There would seem little benefit to setting emission standards for *promising* new sources until the operating characteristics, performance and costs are firmly established. Through cooperation between industry and government, sensible approaches to environmental control need to evolve. The time span to commercialization is a long one. Even for relatively advanced technology, ten to fifteen years elapse. The rules are obsure. For example, it is possible that after a process is completely demonstrated, the fuel would not be acceptable and the billion dollars invested would be wasted. Such an uncertainty represents one of the factors that have discouraged private investment and represents another risk of development. It is a challenge for regulatory bodies to reduce such risks by establishing realistic objectives and permit the development community to develop new technology without such complications.

CONCLUSION

It will require a great deal of joint industry and federal cooperation to develop synthetic fuels technology to a status where the electricity industry will be able to commercialize new methods which are reliable, economic, efficient and environmentally acceptable. The accomplishment of these objectives is no mean task, but one in which the Electric Power Research Institute is playing a significant role.

ACKNOWLEDGMENT

The author wishes to acknowledge the contributions of R. Wolk, N. Holt, and M. Gluckman to this paper. The opinions expressed are those of the author and do not necessarily represent those of the Electric Power Research Institute.

FEDERAL REGULATION OF ATMOSPHERIC EMISSIONS FROM COAL GASIFICATION PLANTS

James F. Durham*

Abstract

The U.S. Environmental Protection Agency's (EPA) intentions regarding the development of standards that regulate the atmospheric emissions from advanced fossil fuel conversion facilities will be outlined. As a further indication of the possible course future Federal regulations will take, the provisions of the statute likely to be used to regulate these emerging industries along with a discussion of the Congressional intent and pertinent judicial decisions concerning the statute will be reviewed. In addition, the factors that must be considered in the development of a standard and the criteria that are used in the selection of sources and pollutants will be discussed. The facilities and pollutants within coal gasification plants that are currently under consideration for standard development will be reviewed. Finally the advantages and disadvantages of the possible standard formats as related to technological capability, monitoring of emissions and determination of compliance will be presented. Hopefully the information presented here will provide guidance to private industry and other government agencies responsible for developing and installing energy conversion processes.

INTRODUCTION

This presentation outlines the U.S. Environmental Protection Agency's (EPA) intentions regarding the development of standards that regulate the atmospheric emissions from advanced fossil fuel conversion facilities such as coal liquefaction or coal gasification plants and oil shale processing facilities. As a further indication of the possible course future Federal regulations will take, the provisions of the statute likely to be used to regulate these emerging industries along with a discussion of the Congressional intent and pertinent judicial decisions concerning the statute are reviewed. The factors that must be considered in the development of a standard, the criteria that are used in the selection of sources and pollutants, and the facilities within coal gasification plants that are currently under consideration for standard development are outlined. In addition, the procedures used to enable interested parties to review and comment on Agency findings prior to formal proposal of regulations in the *Federal Register* are discussed. Hopefully, the information presented will provide guidance to private industry and other government agencies responsible for developing and installing energy conversion processes.

AGENCY INTENTIONS

EPA plans to use Section 111 of the Clean Air Act of 1970, "Standards of Performance for New Stationary Sources"—more commonly called New Source Performance Standards (NSPS), as the primary mechanism for Federal regulation of emissions from emerging industries such as advanced fossil fuel conversion facilities. This decision is consistent with the legislative intent of Section 111 as it is the least costly means of preventing the occurrence of new emission problems. Additional regulation will likely occur through Section 110 of the Act which requires that emissions be maintained at levels that are necessary to comply with the Federal ambient air quality standards or to prevent significant deterioration of the ambient air. It is expected that New Source Performance Standards will reduce future problems in terms of nonuniform State and local regulations. In addition, the regulations and concepts being considered to prevent significant deterioration rely to a significant degree on NSPS to define the best available control technology that can be used to minimize degradation from major new sources.

It is not likely that Section 112 of the Act, "National Emission Standards for Hazardous Pollutants," will be used to regulate advanced fossil fuel conversion facilities. Section 111 provides EPA with a great deal of freedom regarding the type of pollutants that can be regulated provided it is prudent to do so. This would include pollutants that are or could be classified to be hazardous under Section 112 or for which Federal ambient air quality standards exist or are under consideration. Section 111 is particularly attractive for regulating emerging industries because new emission problems can be minimized at a considerable savings in time and resources at the Federal, State, and local level. The savings will result since there will be few if any existing sources to which the standards would be applicable. Therefore, controlling certain pollutants from existing sources as is required under Section 111(d) of the Act will not be necessary. Nor will it be necessary to consider all significant existing sources of hazardous pollutants as would be required under Section 112 of the Act.

---

*The author is with the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

The timely development of NSPS could also result in a considerable savings to organizations responsible for developing and operating advanced fossil fuel conversion facilities. Early direction regarding regulatory requirements will assist in infusing adequate consideration of the environmental factors into the overall assessment of the technical and economic viability of these processes. The environmental problems associated with advanced fossil fuel conversion processes should not be any more difficult to resolve than those encountered in the development of the basic energy conversion process. If such problems do exist and cannot be resolved at a reasonable cost, identification early in the development process will lead to a more rapid assessment of the value of the process and could result in a substantial savings in time and resources. Moreover, new facilities not equipped with best available emission control technology run the risk of eventually having to retrofit the facility due to possible changes in State and local regulations. Such retrofit costs are in general significantly more expensive than installing the control equipment at the time of construction.

Considering the nation's current concern for the environment, it is unlikely that advanced fossil fuel conversion processes will reach commercialization without being reasonably certain that significant environmental problems will not be created and that all reasonable precautions have been taken to ensure that emissions to the environment have been minimized. A detailed EPA assessment of what can be done to minimize emissions could lead to a more rapid acquisition of the necessary State construction and operating permits and Federal agency approvals; will tend to satisfy environmental groups; and will assist in obtaining the necessary financing.

There are many advanced fossil fuel conversion processes currently under development—most in the early stages of development. Thus, there is ample time to adequately assess the environmental considerations without delaying the commercialization of the most promising processes. It is possible that some processes currently under development may be terminated due to environmental considerations; however, such termination would be in the best national interest and should not be construed to mean that EPA is delaying the nation's goal of achieving energy independence.

Therefore, as the regulatory body responsible for insuring that new emission problems are prevented, the Emission Standards and Engineering Division with EPA will continue to review the environmental problems associated with advanced fossil fuel conversion facilities and to develop standards (as sufficient information becomes available) consistent with the legal provisions and the Congressional intent of Section 111.

PROVISIONS AND CONGRESSIONAL INTENT

Section 111 of the Act requires the establishment of standards of performance for new stationary sources that " . . . may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare." The Act requires that standards of performance for such sources reflect " . . . the degree of emission limitation achievable through the application of the best system of emission reduction which (taking into account the cost of achieving such reduction) the Administrator determines has been adequately demonstrated."

The overriding purpose of performance standards for new stationary sources is to prevent the occurrence of new air pollution problems. In establishing Section 111, Congress also sought to maintain existing high quality air and to ensure uniform national standards for new facilities within the various stationary source categories. As indicated below, the purpose of NSPS is clearly stated in the legislative history of the Clean Air Act (ref. 1).

". . . We must also guard against new problems. Those areas which have levels of air quality which are better than the national standards should not find their air quality degraded by the construction of new sources.

"These new source performance standards would require industry to apply the latest available emission control technology and processes wherever a new plant is located . . . . The concept is that wherever we can afford or require new construction, we should expect to pay the cost of using the best available technology to prevent pollution.

"Maintenance of existing high quality air is assured through provision for maximum control of new major pollution sources.

"Perhaps one of the most significant provisions in the bill deals with the establishment of Federal emission standards for new stationary sources. . . . The purpose of this new authority is to prevent the occurrence anywhere in the United States significant new air pollution

problems arising from such sources either because they generate extra hazardous pollutants or because they are large scale polluters."

Congress intended that regulated stationary source categories would be designed, constructed, equipped, and maintained so as to reduce atmospheric emissions to a minimum. It prescribed that such standards be expressed as emission limits, thus enabling the owner or operator to select the most economical and acceptable means of achieving them. These would include process changes, operational changes, and direct emission controls, as well as any other practical method.

Congress also intended that NSPS be applied to modified sources when such modifications result in increased air pollution emissions. Such modifications have been generally defined as a process or raw material change that results in an increase in emissions.

Standards of performance were not viewed as being static. Congress foresaw the need for continued review of existing standards, and the promulgation of revised standards as new technology or operating methods emerged.

Congress also provided that the Administrator in establishing standards of performance would determine the degree of control that has been or can be achieved by means of technology that is or can be made available. Congress prescribed that such a determination must be reasonable in terms of the cost of such technology, and in the time of its availability.

Within the framework of congressional intent, a number of general concepts that serve to foster the review of recommended standards of performance and the support rationale have been derived. These are briefly set forth below:

1. Individual standards are not intended to be protective of health or welfare effects; that is, they are not designed to achieve any air quality goals. The standards are designed to reflect best technology for each individual source. The long-range goal and overriding purpose of the collective body of standards is to prevent new pollution problems from developing. To achieve this end, the standards must force technological change and the justification for the standards must allow for technology transfer.

2. Because the standards attempt to define the best systems of emission reduction, the data base upon which the standards are justified will necessarily be limited. Test data on existing well-controlled plants are the most desirable basis for setting emission limits for new plants. Since the control of existing plants generally represents retrofit technology, or is designed to meet some existing State/local regulation, even those levels are subject to improvement. Therefore, the Administrator's judgment is necessarily involved in every proposed standard, even when the data base is "adequate."

3. There are no waiver provisions for standards of performance. Unlike State/local agencies, EPA does not have a mechanism to waive the standards when a source has made a good faith effort to comply but misses the mark by some amount. Short of not allowing the source to operate, EPA can: (a) neglect to enforce the standard, since use of enforcement authority is discretionary; or (b) issue an order that would provide the source some finite time to improve the control system to achieve the standards. Both the options are subject to policy changes. Therefore, the standards must be set so the probability of compliance is high. This, of course, is contradictory with the mandate to set standards that force technology.

CLARIFYING JUDICIAL OPINIONS

The intent of Congress, and the resultant legislative language, has been further clarified by court opinions emanating from litigation over promulgated standards of performance. The Federal Court of Appeals, District of Columbia Circuit has found that: (1) EPA is required to consider costs in terms of counter-productive environmental effects as well as the economic impact upon the industry. (2) EPA is not required to perform a cost-benefit analysis comparing benefits derived from reduced emissions with those costs associated with control. (3) The court makes it clear that it is sufficient for EPA to show that a standard can be achieved rather than that it has been achieved. The essential consideration is that there will be technology available for installation in new plants (ref. 2).

". . . Section 111 looks toward what may fairly be projected for the regulated future, rather than the state of the art at present, since it is addressed to standards for new plants . . . The essential question was rather whether the technology would be available for installation in new plants. . . . the question of availability is partially dependent on 'lead time,' the time in which the technology will have to be available. Since the standards here put into effect will control new plants immediately, as opposed to one or two years in the future, the latitude of projection is correspondingly narrowed. If actual tests are not relied on, but instead a prediction is made, 'its validity as applied to this case rests on the reliability of [the] assumptions' . . ."

The extent to which EPA must demonstrate achievability was expanded upon in a second opinion when the Court held that

"It is the system which must be adequately demonstrated and the standard which must be achievable. This does not require that a sulfuric acid plant be currently in operation which can at all times and under all circumstances meet the standards, nor, however, does it allow the EPA to set the standards solely on the basis of its subjective understanding of the problem or 'crystal ball' inquiry. . . . An adequately demonstrated system is one which has been shown to be reasonably reliable, reasonably efficient and which can reasonably be expected to serve the interests of pollution control without becoming exorbitantly costly in an economic or environmental way. An achievable standard is one which is within the realm of the adequately demonstrated system's efficiency and which, while not at a level that is purely theoretical or experimental, need not necessarily be routinely achieved within the industry prior to its adoption (ref. 3)."

SELECTION OF SOURCES AND POLLUTANTS

Selection of sources and pollutants for standard development is based to a significant degree on the anticipated reduction in the mass rate of emission that can be derived from the standard. This emission reduction (benefit) is estimated from the emission rates that can be achieved through the application of available control techniques. Generally, two or three control techniques or processing schemes that cover a range from average control to best control will be evaluated. Existing State and local regulations and "average" control levels are used to determine the reduction in the rate of emissions that would result from applying this technology. The estimated number and size of new and replacement facilities are then used to calculate the emission reductions that can be expected in future years (ref. 4).

Other factors are also weighed in the selection of sources and pollutants. For example, emphasis is currently on the development of standards for hydrocarbons and nitrogen oxides. Although it appears that most areas of the country are in compliance with the Federal ambient air quality standard for NO_2, many cities are near the standard. Standards that require new sources to install best demonstrated technology will minimize the effect of growth on ambient air quality.

A recent internal report shows that the ambient air quality oxidant standard will not be maintained in many urban areas without increased control of stationary sources (ref. 5). It is becoming obvious that maximum control of all hydrocarbon sources nationwide is the only way to handle the oxidant problem.

Recent findings have additional implications for control of the nonurban oxidants problem. Both the more reactive and less reactive organics, under the conditions of light winds associated with persistent high pressure systems, may have sufficient time to generate oxidants. Thus, reduction of total emissions and not just reduction of the more reactive compounds would need to be emphasized in nonurban areas. Control of organic rather than nitrogen oxide emissions appears to be the most effective route to reduce oxidant levels in rural areas. However, to attain the standard, coordination of both organic and nitrogen oxides emission control may be necessary (ref. 6).

Additional benefits that can be derived from a standard, such as heat or resource recovery or the reduction of toxic metals, carcinogens, or other hazardous materials are also considered in the selection process.

GENERAL APPROACH FOR COAL GASIFICATION PLANTS

Before standards are promulgated, EPA must establish the magnitude of the emission problem, identify the technology available to reduce the emissions, and identify the emission levels and emission reductions that would result from the application of that technology. In addition, the penalties associated with the technology, such as investment and operating costs, economic impact on the industry, consumption of energy or other natural resources, and adverse environmental problems, must be defined. The Agency must then determine if these factors are reasonable. Information obtained from foreign companies operating coal gasification facilities, from EPA contractor studies and from U.S. companies that are planning to install full-scale commercial coal gasification facilities is being used to assess these factors. The Agency is relying heavily on the detailed engineering and thought that has gone into the proposed U.S. installations.

Our initial standards for coal gasification plants will likely focus on restricting the atmospheric emissions of the gaseous sulfur compounds and non-methane hydrocarbons formed in the gasifiers. The potential emissions are significant and there appears to be adequate information available to identify emission levels that can be achieved with available technology.

The procedures that are followed during the course of the standard development program provide ample time to enable industry, environmental groups and other interested parties to prepare substantive comments on the Agency's initial conclusions well before proposed regulations are placed in the *Federal Register*.

A Standard Support Environmental Impact Statement (SSEIS) will be prepared that contains the Agency's findings concerning the technology that is considered demonstrated, the emission levels that can be achieved and the environmental and economic costs of applying the technology. The document will be distributed to the National Air Pollution Control Techniques Advisory Committee* (NAPCTAC), to industry trade associations and other interested parties along with the Agency's preliminary recommendations. Approximately one month after distribution of the SSEIS, it will be reviewed in an announced public meeting with the National Air Pollution Control Techniques Advisory Committee. Comments received at the NAPCTAC meeting are given serious consideration before proposed standards are prepared for publication in the *Federal Register*.

SUMMARY

EPA intends to vigorously proceed with the development of standards to regulate the atmospheric emissions from advanced fossil fuel conversion facilities. Regulation of these emerging industries will likely be implemented through Section 111 of the Clean Air Act of 1970, "Standards of Performance for New Stationary Sources." The overriding purpose of standards of performance is to prevent the occurrence of new air pollution problems. Standards will be developed as information becomes available that satisfies the legal provisions and Congressional intent of Section 111.

Early direction regarding the regulatory requirements for advanced fossil fuel conversion facilities will provide incentive to adequately consider environmental factors in the overall assessment of the technical and economic viability of advanced fossil fuel conversion facilities. Identification of serious environmental problems early in the development process is in the best national interest since it could result in a substantial savings in time and resources.

The majority of the fuel conversion processes are in the early stages of development. Thus, there is ample time to consider environmental factors without delaying the nation's goal of achieving energy independence.

Review of the provisions of Section 111, the Congressional intent of the statute, and the pertinent judicial decisions indicates that EPA must demonstrate that a new source performance standard can be achieved, that the technology is available, and that the resulting costs, economic impact, energy consumption, and adverse environmental effects are reasonable when compared to the reduction in atmospheric emissions that will occur. Thus, EPA efforts will be directed toward identifying and basing standards on processes or techniques that can achieve the lowest emission levels consistent with reasonable cost in terms of dollars, energy consumption, and adverse environmental penalties.

Consideration of the Congressional intent and legal provisions of Section 111 should provide substantive guidance regarding future Federal regulatory requirements to those responsible for developing, designing, and operating advanced fossil fuel conversion processes.

A major factor used to select sources and pollutants for standard development is the resulting reduction in the mass rate of emissions from new or replacement facilities. Pollutant selection is also based on the effect the standards would have on maintaining or achieving the Federal ambient air quality standards. Additional factors considered include the prevention of significant deterioration of air quality, the reduction of highly toxic materials, and the energy savings that would result from a standard.

Since available data will be more limited for emerging industries, more engineering judgment and translation of technology from other application areas will be required than has been used in the past on more established industries. As a result, early standards will likely contain more "cushion" to allow for the increased uncertainty.

REFERENCES

1. "A Legislative History of the Clean Air Amendments of 1970," Serial No. 93-18 (GPO, January 1974), pp. 227, 260, 402, and 816.
2. Portland Cement Association vs. Ruckelshaus, Medusa Portland Cement Co., et al., 486 S.2d 375, July 29, 1973.
3. Essex Chemical Corporation, et al., vs. Ruckelshaus, Appalachian Power Company, et al., vs. EPA, 486 F.2d 427, September 10, 1973.
4. TRC, The Research Corporation of New England, "Impact of New Source Performance Standards on 1985 National Emissions from Stationary Sources." Volume I, EPA Contract 68-02-1382, Task No. 3, October 24, 1975.†

---

*An advisory group established pursuant to sections 108(b)(1) and (2) and 117(f) of the Clean Air Act as amended. The Committee advises on information documents regarding air pollution control techniques and testing and monitoring methodology for categories of new sources and air pollutants subject to the provisions of Sections 111 and 112 of the Clean Air Act as amended.

†The procedures used by TRC were developed by Mr. George W. Walsh, Assistant to the Director, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

5. U.S. Environmental Protection Agency, Office of Air and Waste Management, "Air Quality Impact of Alternative Emission Standards for Light Vehicles," p. 1, March 4, 1975, Revised March 12, 1975.

6. U.S. Environmental Protection Agency, Office of Air and Waste Management, Office of Air Quality Planning and Standards, "Control of Photochemical Oxidants—Technical Basis and Implications of Recent Findings," EPA-450/2-75-005, July 1975.

SUMMARY OF MULTIMEDIA STANDARDS

John G. Cleland*

Abstract

While sulfur control in the atmosphere is presently of major concern to synthetic fuel plants, other pollutants such as those affecting water quality, solid waste, and other substances emitted into the air (especially organic carcinogens and toxic trace metals) must also be controlled. This discussion summarizes existing State and Federal multimedia regulations, the rationale and processes for the developing standards, and possible legal trends applying to the synthetic fuel industry. EPA-RTP has recently assumed responsibility for assessment and control of effluents in all media for this industry. In the absence of specific standards for fuel conversion, application and extrapolation of standards for other industries are examined.

At this time, a discussion of environmental regulations entitled "Multi-Media Standards" is a misrepresentation of facts. While pollutants in all media—air, water, land—have been addressed by standards, there is no lone standard which limits any pollutant in every medium. The regulations fostered by the former Atomic Energy Commission (AEC) pertaining simultaneously to radionuclides in both air and water may be closest to a multimedia standard.

The question of whether such inclusive standards should be formulated has been raised at various times. Without resort to technical arguments, it can be simply stated that many complications make the probability of multimedia standards unlikely. For instance,

1. Addressing all media effluents from a particular industry under a single standard is possible, but regulations and methods for their implementation would have to be restructured;
2. Controlling any pollutant in all media by a single regulation is virtually impossible because of dissimilar monitoring and analysis, different toxic effects and synergistics, and different control technology for substances in varying streams.

There has been a great deal of difficulty encountered in attempting to correlate standards applied to the same medium.

A recent report (ref. 1) analytically examined the problem of cross-media interaction, e.g., a cooling system for controlling thermal water pollution may adversely affect local air quality. Table 1 illustrates an included comparison of the importance or consideration which should be given to each medium. The expert opinion column was derived through a survey of EPA personnel. Those opinions were coupled with selected regional characteristics and ultimate weights assigned by a statistical computer model.

The second column was obtained by further adjusting by total damage or treatment costs so called "social costs," i.e., dollars. In the final analysis, "the proof is in the pudding."

Table 1. Estimates of media weights

	Expert opinion	Social costs
Air	290	540
Water	390	290
Land	320	170
	1000	1000

Using another yardstick, EPA says it took four times as many enforcement actions in its second 2 years, 1972-1974, as in its first 2: about 8 percent of the actions were for air emissions from stationary sources; 9 percent for stationary source water effluents; 20 percent for oil spills; and 60 percent for pesticides. Solid waste disposal is not enforced. Ford Motor Company picked up $7 million of the total $8.7 million tab in fines levied.

Some justification for concern about the environmental impact of synthetic fuel plants is seen in table 2. The tonnages are a very rough projection (ref. 2) for a total of 100 plants. By the year 2000, enough waste could have accumulated to cover all of Rhode Island a foot deep in ash and sulfur.

Table 3 shows reasonably comprehensive standards which may be of interest to coal conversion planners. While certainly new source performance standards for fossil fuel conversion facilities are forthcoming (ref. 3), other regulations are only in embryonic stages.

State implementation plans are those designed to meet EPA Air Quality standards under the Clean Air

---

*The author is with the Energy and Environmental Research Division of the Research Triangle Institute, Research Triangle Park, North Carolina.

Table 2. EPA estimate of potential pollutants from synthetic fuel

Pollutant	Tons/yr[1]	Accumulated 1980-2000[2]
Sulfur	36,000,000	327,000,000
Nitrogen (fuel)	14,000,000	130,000,000
Ash	150,000,000	1,330,000,000
Ammonia	35,000,000	318,000,000
Tars, oil	21,000,000	191,000,000
Waste water	683,000,000	6,209,000,000
Chlorine	1,300,000	12,000,000
Vanadium	35,000	318,000
Flourine	66,000	600,000
Bromine	17,000	155,000
Arsenic	15,000	136,000

[1] Basis: Year 2000, total tons of coal 1.1×10^9 tons/yr

[2] 10×10^9 tons of coal

Table 3. Pollutant regulations

Air	Water	Land
Ambient air quality standards	Receiving water quality standards	State and local standards
State and local standards (Implementation plans)	State and local standards	Incentives Solid waste disposal act Resource recovery act
National primary standards	Drinking water standards	
National secondary standards	U.S. Public Health Service	AEC radioactive disposal
Nondegradation standards	EPA	
Source emission standards	Effluent limitations	MESA regulations
Source and local standards	State and local standards	
New source performance standards	New source performance standards	
Hazardous pollutants	Best practicable technology currently available	
Workroom atmosphere	Best available technology economically achievable	
OSHA		
TLV's-ACGIH	Pretreatment standards	
	Zero discharge	
	Hazardous substances	
	AEC radioactive	

Table 4. Excerpts-applicable national pollutant regulations

Substance	Air quality standards mg/m^3	NSPS lb/10^6 Btu	Workroom mg/m^3	Effluent standards lb/1000 lb 30 day avg.	Drinking water standards mg/liter
Ammonia			18		
CO	10		55		
Hydrocarbons	0.16 Nonmethane		360		
H_2S			15		
NO_X, nitrates	0.1 (NO_2)	0.7	9		10 (nitrate)
Particulates	0.075	0.19	10		
Phenols			19	0.2	0.001
SO_2, sulfates	0.08 (SO_2)	1.2	13 (SO_2)		250

Act. Many have been revised from the original national standard attainment date of July 1975 to later dates, such as 1977.

The States' Receiving Quality Standards comprise implementation plans for water. But Federal water quality regulations are not as quantitative as those for air. They specify control methods—"Best Practicable Technology" by 1977 and "Best Economically Achievable Technology" by 1983. Pretreatment applies to discharges to municipal sewers. Zero discharge criteria for aqueous effluents are based on the stipulation that discharge cannot contain higher pollutant levels than intake streams. Some relaxation of "zero" discharge may be available because of the industrial quality of intake water.

There are no Federal statutory limitations on solid waste disposal in the public sector. The incentive legislation listed provides only for Federal research, demonstrations, training and technical assistance. Most state standards are concerned primarily with municipal disposal. The Mining Enforcement and Safety Administration has added more stringent requirements for coal refuse banks and the disposal of mine spoils, especially since the Buffalo Creek disaster.

There are Federal standards which are applicable to synthetic fuel plants at present: The New Source Performance Standards (NSPS) reflected in table 4 are for coal-fired steam generators. The American Conference of Governmental Industrial Hygenists (ACGIH) and the Occupational Safety and Health Administration (OSHA) publish enforceable regulations in the form of threshold limit values (TLV's) for substances in industrial air. The limits are usually for 8-hour exposure periods and along with the National Institute of Occupational Safety and Health (NIOSH) Toxic Substances List have been used in various analyses for proper environmental assessment. OSHA and ACGIH also have established limits for physical agents such as noise and have prohibited the presence of determined carcinogens.

There is only one effluent limit shown—for phenol—but the effluent standards also include such water parameters as BOD5, COD, TSS and pH for new sources. About 38 industries or categories are already included under the EPA effluent standards, and synthetic fuels processes are a possible addition.

Selected air and water pollutants (table 5) are commonly addressed by the individual States. These average standards are for all States having pertinent regulations. Where the average is higher than the corresponding Federal regulation—such as for SO_X and particulates—legal exceptions have been made for certain equipment types or locations.

Some State standards are much more stringent than Federal—for instance, the only State with an emissions plan for gasification plants, New Mexico, proposes less than one-third the allowance of particulates given by the NSPS for coal-fired generators.

It should be remembered that standards which are not directly applicable to fuel conversion may have the greatest impact on the industry—such as strip mining legislation.

More detailed summaries of then existing environmental standards are given in the combination of several fine papers (refs. 4,5,6,7) offered at the last Synthetic

Table 5. Selected averaged State regulations

Pollutant	Mean standard for states
Particulates	
New fuel burning (10^3 Btu/hr	.19 lb/10^6 Btu
Industrial processes (>500 tph)	52.8 lb/hr
Sulfur oxides	
New fuel burning (solid fuel)	1.25 lb/10^6 Btu
Sulfur recovery plants	.06 lb/lb S
Nitrogen oxides	
Coal-fired combustion	.70 lb/10^6 Btu
Hydrocarbons	85-90% reduction of all emissions over 15 lb/day
NO_3	41.5 mg/l
Ammonia, NH_3	2.2 mg/l
Chromium	.08 mg/l
Manganese	.37 mg/l
Δ Temperature (Maximum)	5.1°F
Maximum pH	8.86

Fuels Symposium. One of these, by Rubin and McMichael (ref. 7), includes a brief analysis of some implications of existing emission and effluent regulations.

Table 6 shows effluent standards adjusted to the same units for two industries which are often compared to coal gasification and liquefaction plants. It will be noted that the limits approximate one another.

More relevantly, table 7 includes effluents for the same refineries and coking plants and also for coal conversion plants in a six-State region. Effluents are based on estimates of 22 percent of U.S. crude oil flow and 63 percent of U.S. coke produced in this region. Applying the effluent regulations for coke plants to coal conversion plants, it was found that six 20,000 lb coal/day conversion plants would put out a comparable weight of effluents.

While this sort of extrapolation may be helpful to designers of U.S. synthetic fuel complexes, it is emphasized that planners should attempt to keep abreast of new proposals and possible legislation in the environmental field. There have been no environmental regulatory actions taken in the year and a half since the last fuel conversion symposium which might significantly change the course of the industry. Table 8, however, does list a few events which could have effect.

EPA recently denied a relaxation of its SO_2 standard for those with the problem of sludge from lime scrubbers in fossil fuel-fired steam generation plants. However, a change in the particulate opacity measurement methods was allowed.

The House Interstate and Foreign Commerce Subcommittee submitted on September 5, 1975, its draft on prevention of "significant deterioration" in clean air (nondegradation) areas. These proposed rules are tougher than those discussed at the May 1974 symposium in St. Louis and have been extended from just SO_2 and particulates to all air pollutants covered by the Ambient Air Quality Standards, i.e., CO, oxidants, hydrocarbons and NO_2. For synthetic fuel plants contemplating locating in areas of the country where clean air quality

Table 6. Adjusted new source performance standards (pounds of pollutant per 10^{12} Btu feedstock, 30-day manixum)*

Pollutant	Petroleum refineries	By-product coke making
BOD_5	230-1015	477
TSS	143-646	242
Ammonia (as N)	46-400	242
Oil and grease	71-233	12
Phenols	1.5-7.1	5.8
Sulfide	1.2-6.8	

*Assumes heating values of 6.5 MMBtu/bbl for crude oil and 12,000 Btu/lb for coal, with a coke yield of 0.69 lb coke/lb coal.

Table 7. Estimated total wastewater emissions of selected pollutants for six major eastern coal states (pounds per day based on 30-day average NSPS limits)

Pollutant	Refineries*	Coke plants**	Coal conversion plants***
Phenols	30-138	38	33
Ammonia	900-7,800	1636	1378
BOD_5	4,800-148,000	2910	2756
TSS	2,790-12,800	1636	1378
Oil and grease	1,380-6,300	1638	1378

* Assumes 22 percent of U.S. crude flow processed in the six-state region.

**Assumes 63 percent of U.S.by-product coke processed in the six-state region.

***Assumes six 20,000 ton/day plants operating NSPS limits for coke plants over the six-state region.

already exceeds standards, the deterioration limits may present the most formidable constraint.

1974 New Source Performance Standards produced are:

1. A particulate standard of 0.070 g/dscm for coal preparation plants;
2. Monitoring methods for all designated new and modified plants; sources required to install continuous monitoring instruments of proscribed performance and report data to State agencies quarterly; and
3. Proposed air emission and water effluent limitations for railroad operations such as cleaning, draining and maintenance.

Table 8. Recent regulatory activities

1975

Implementation plan – primary drinking water standards
No revision – NSPS – fossil fuel generators
House subcommittee draft – degradation
NIOSH recommendation – arsenic, .002 mg/m^3

1974

NSPS – coal preparation plants
NSPS – monitoring and testing
Proposed regulations – hazardous substances
Draft recommendation – effluents and NSPS, railroad operations

More than 350 chemical compounds may be designated as hazardous pollutants and regulations set. Civil penalties would be imposed for discharges of substances determined to be "not actually removable." The last known "optimistic" date for finalization was published as September 1975.

Finally, EPA program managers in synthetic fuels recently made a very preliminary assessment of pertinent effluents (table 9) which are likely to be controlled by standards. No timetable is proffered. Preliminary *Standards of Practice Manuals* with a minimum of new data may be issued by EPA within the next year. However, standards setting–especially for water and land effluents and for nonambient air quality emissions–is certainly lagging technology. A reliable data base is required. Provision of this data base to environmental agencies by industry and researchers in the field and a reciprocal inclusion of industry in the standards setting process is obviously the most expedient and satisfactory method for insuring environmentally sound fuel conversion technology.

Table 9. Prediction of new EPA standards for synthetic fuels

Effluents standards likely	Control technology	
	Available	R & D required
Airborne		
Fugitive dust	Yes	No
Sulfur, oxidized	Yes	No
Sulfur, reduced	Yes	Yes
Nitrogen, oxidized	No	Yes
Nitrogen, reduced	Yes	Yes
Carbon monoxide	Yes	No
Hydrocarbons, storage	Yes	No
Particulate ash	Yes	No
Noise	Yes	Yes
Aqueous		
Storage pile runoff	Yes	Yes
Sour water/preparation	Yes	No
Sour water/process	Yes	Yes
Slurry transportation	Yes	No
Thermal	Yes	Yes
Solid & sludges		
Water treatment sludge	Yes	Yes

REFERENCES

1. "Development of Cross-Media Evaluation Methodology," prepared for Environmental Quality Council by Battelle Columbus Laboratories, NTIS No. PB-232414, 15 January 1974.
2. *Project Independence*, FEA Final Task Force Report, FE 1.18:G29, November 1974.
3. James F. Durham, EPA presentation on "Federal Regulation of Atmospheric Emissions for Advanced Fossil Fuel Conversion Facilities," Advanced Fossil Fuel Sector Group Meeting, EPA-RTP, 13 November 1975.
4. Jack R. Farmer, "Environmental Quality and Standards for Air," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, EPA-650/2-74-118, May 1974.
5. Kenneth M. Mackenthun, "Environmental Quality and Standards for Water," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, EPA-650/2-74-118, May 1974.
6. A. Blakeman Early, "Coal Conversion Technology and Solid Waste Disposal: Time to Take Stock," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, EPA-650/2-74-118, May 1974.
7. E. S. Rubin and F. C. McMichael, "Some Implications of Environmental Regulatory Activities on Coal Conversion Processes," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, EPA-650/2-74-118, May 1974.

AN INVESTIGATION OF TRACE ELEMENTS IN COAL

H. J. Gluskoter, R. A. Cahil, W. G. Miller,
R. R. Ruch, and N. F. Shimp[*]

Abstract

A variety of coal samples is currently being extensively analyzed for constituents, including many trace elements, at the Illinois State Geological Survey. The samples include whole coals, washed coals, and bench samples. Among the many determinations made on each sample are analyses for approximately 60 elements, almost twice the number of elements previously determined. The increase is in part the result of the addition of instrumental neutron activation analysis (INAA) equipment to the laboratory.

Twenty-five samples of Herrin (No. 6) Coal that had been analyzed previously were subjected to INAA analysis and were found to include Ba, Ce, Cs, Dy, Eu, Au, Hf, I, In, La, Lu, Rb, Sm, Sc, Ag, Sr, Ta, Tb, Th, W, U, and Yb, none of which were reported by previous techniques. These elements generally are present in very small amounts and, with the exception of barium, exhibit no wide range in concentration. The rare earth elements are among those having the narrowest ranges.

Wide variations in element content have been observed in bench sets of coals (samples of vertical segments of the coal seam). Many elements, notably germanium, are concentrated at the top and/or bottom of the seam, the high concentrations of Ge being found there in all four bench sets analyzed to date.

INTRODUCTION

Research concerning the modes of occurrence and distribution of trace elements in coals has been intensively conducted at the Illinois State Geological Survey for the past six years and has resulted in the publication of a number of reports. Included among the more substantive of these are three that were published in the Illinois State Geological Survey's Environmental Geology Notes series (refs. 1-3). The most recent of these EGN's was also distributed by the U.S. Environmental Protection Agency.

In this short report, an attempt is made to update this continuing research, summarize new or significantly modified analytical techniques, and present some very recent—although still preliminary, data on the distribution of elements that we have not previously determined in coals and on the vertical distribution of trace elements throughout the coal seam. A more complete discussion of these data must await the completion of the chemical analyses of the current group of samples, but we hope it will be published in a series of papers within the next year.

Obtaining data concerning the distribution and mode of occurrence of trace elements in coals is an obvious first step in assessing the environmental aspects of fuel conversion, the subject of this symposium. It has not, however, always been among the first steps taken. Not only are trace element data essential for determining potential environmental effects of coal conversion processes, but they are also needed for assessing which materials recoverable from coal conversion plants have possible economic importance, and for predicting the potential effects, both positive and negative, these elements may have on catalytic reactions involved in the conversion processes.

Research reported here and in the publications previously mentioned (refs. 1-3) was supported in part by Contracts 68-02-0246 and 68-02-1472, and Grant R800059 from the U.S. Environmental Protection Agency, Energy Assessment and Control Division, Fuel Process Branch, Research Triangle Park, North Carolina.

CURRENT INVESTIGATIONS OF TRACE ELEMENTS IN COAL

Previous investigations of trace elements in coal at the Illinois State Geological Survey have been reported in several publications within the past year and a half. Those reports presented data on chemical analyses of 101 whole coal samples and 32 samples of washed coals (separated by specific gravity in the laboratory) and summarized the geochemical significance of those data (refs. 2-4). Thirty-three elements were determined for each sample, in addition to normal coal parameters, in the original investigations. Our current investigations are expanding the previous study by the analyses of additional whole coal samples, washed coal samples, and bench samples, and also by determining many more elements in a series of 25 samples of Herrin (No. 6) Coal from Illinois. The latter coal samples had previously been analyzed for the original 33 elements.

Seventy additional whole coal samples are being analyzed. Of these, 31 are from the Illinois Basin (Illinois, southwestern Indiana, and western Kentucky), 14

---

[*] The authors are with the Illinois State Geological Survey, Urbana, Illinois 61801.

are from eastern states, 22 from western states, and 3 are from Iowa. These samples are all face-channel samples or composite face-channel samples made by combining individual face-channel samples. Most of them were collected by Illinois State Geological Survey personnel.

Several sets of washed coals also are being analyzed. In the laboratory they have been separated into fractions based on specific gravities, and each fraction has been chemically analyzed. At least five sets, comprising more than 35 total samples, are to be tested: three coals from Appalachian coal fields (Alabama and northern and southern West Virginia), one from Illinois, and one from Arizona.

Other coal samples have been collected by sampling the coal seam in vertical segments or "benches." Four sets, consisting of a total of 33 bench samples, have been collected from the Herrin (No. 6) Coal in Illinois. The sets are from sites that have been judged to be significantly different from each other with respect to their geological setting in the Illinois Basin.

All the coal samples have now been analyzed for approximately 60 major, minor, and trace elements, in addition to carbon, hydrogen, oxygen, and nitrogen, which are included in the standard "ultimate" analysis of coal.

Determination of such a large number of elements in the current series of analyses is now possible because within the past few years, we have significantly enlarged our capabilities for determining trace and minor elements in coal. Table 1 shows the procedures now available and the elements they detect. The major addition has been instrumental neutron activation analysis (INAA), in which a high-resolution Ge(Li) detector is used. The technique can provide accurate, precise values for some 38 elements. The method uses whole coal as the sample without ashing or dissolution and thus avoids volatilization losses. In the procedure, the whole coal samples are irradiated in the University of Illinois TRIGA MK II nuclear reactor facility, counted on the 10 percent Ge(Li) detector coupled to a 4096 multichannel analyzer, and compared to a multielement composite standard, which has been treated identically. To exploit adequately all the nuclear properties and parameters available for neutron activation, a combination of

Table 1. Analytical procedures used in coal analysis

Procedure	Type of sample	Element
Instrumental neutron activation analysis (INAA)	Whole coal	Na*, K*, Rb, Cs, Sr*, Ba, Ga, In, As, Sb, Se, Cl*, Br*, I, Sc, V*, Cr*, Mn*, Co*, Fe*, Ni*, Zn*, Mo*, Ag*, Hf, Ta, W, Au, La, Ce, Sm, Eu, Tb, Dy, Yb, Lu, Th, U
Neutron Activation Analysis-Radiochemical seperation (NAA(RC))	Whole coal Low-temperature ash (150°C)	Hg Te†
X-ray flourescence-wave-length dispersion (XRF)	Whole coal	Na*, K*, Mg, Ca, Al, Si, S, P, Cl*, Br*, Ti, Ni*, Zn*, Fe*
Atomic absorption (AA)	Low-temperature ash (150°C)	Ni*, Cu*, Zn*, Cd*, Pb*, Tl†, Li†
Optical emission-direct reader (OED)	High-temperature ash (500°C)	Be, Sr*, B, Ge*, V*, Cr*, Co*, Cd*, Ni*, Cu*, Zn*, Zr*, Mo*
Optical emission-photographic (OEP)	High-temperature ash (500°C)	Ge*, Pb*, V*, Cr*, Co*, Ni*, Cu*, Mn*, Zn*, Zr*, Mo*, Ag*, Sn†
Ion-selective electrode (ISE)	Whole coal	F

*Elements for which two or more analytical procedures have been applied.

†Elements for which further methods of analysis are being developed.

different irradiation and counting periods is used. This method is much superior to the previously used instrumental approach that employed the low-resolution NaI(Tl) detector. INAA also essentially eliminates some previously required, tedious radiochemical separations for Sb, Se, As, and Ga. Radiochemical separations—NAA(RC)—are still required, however, to get adequate analysis for Hg.

X-ray fluorescence wave-length dispersive (XRF), atomic absorption (AA), optical emission-direct reading (OED), and ion-selective electrode (ISE) techniques all have been upgraded and refined during the present project.

An energy-dispersive X-ray fluorescence technique, which employs a high-resolution Si(Li) detector, isotopic source (^{241}Am), and secondary metal foils for sample excitation, is currently being developed at ISGS for future used in determining up to 20 elements in whole coal samples.

RECENT DATA

Two groups of data will be included in the brief discussion to follow. The first group concerns 22 additional elements determined on samples previously analyzed, and the second group concerns the trace-element distribution in bench samples. All of the values presented here should be considered as preliminary and, although we are confident that most of them will not be changed prior to publication of the final values, a few changes may be made. This disclaimer is necessary so that we might present data obtained so recently that we have not yet had time to make all the usual tests for accuracy, both analytical and clerical.

Additional Elements Determined in Coals

Ruch et al. (ref. 3) reported in 1974 the analyses of 101 whole coal samples. Trace elements determined on each of these samples were antimony, arsenic, beryllium, boron, bromine, cadmium, chromium, cobalt, copper, fluorine, gallium, germanium, lead, manganese, mercury, molybdenum, nickel, phosphorus, selenium, tin, vanadium, zinc, and zirconium. In addition, the following major and minor elements were also determined: aluminum, calcium, chlorine, iron, magnesium, potassium, silicon, sodium, sulfur, and titanium. Standard coal analyses—i.e., proximate, ultimate, heating value, varieties of sulfur, and ash also were reported.

Twenty-five of the 101 coal samples, from the Herrin (No. 6) Coal in the Illinois Basin, have been analyzed further, and the following trace elements have been determined: barium, cerium, cesium, dysprosium, europium, gold, hafnium, iodine, indium, lanthanum, lutecium, rubidium, samarium, scandium, silver, strontium, tantalum, terbium, thorium, tungsten, uranium, and ytterbium. These elements were determined primarily by instrumental neutron activation analyses, although corroborative analyses made by other methods were obtained for some elements (table 1).

The data from the analyses of the 25 coals are summarized in table 2. Arithmetic mean, standard deviation, and range of elemental concentrations (minimum and maximum) are given for each element. For all these elements, the standard deviations from the mean are less than or equal to the arithmetic mean, with the exception of those for barium and silver. This is another way of stating that the range in values for these elements is rather narrow. Among those elements with narrower ranges in values are rubidium, cesium, hafnium, tantalum, and the lanthanides (La, Ce, Eu, Tb, Dy, Yb, and Lu). In previous reports (refs. 3 and 4), we have noted that those elements that occur in discrete mineral phases in the mineral matter of the coal are those that exhibit the widest ranges in concentration of the elements and the largest standard deviations relative to their arithmetic means. The mineral barite ($BaSO_4$) has been observed in coals from several localities in Illinois, which is a reasonable explanation for some very high barium concentrations in coals from the Illinois Basin. Relatively wide ranges also were observed for the chalcophile elements, those elements that commonly occur in nature as sulfides. Silver is a chalcophile element and may also be found in very limited amounts in solid solution in pyrite (FeS_2) and/or in marcasite (FeS_2).

Analyses of Bench Samples

In an attempt to determine the vertical variation in trace elements within coal seams, we have collected, and are still collecting, sets of samples called bench samples. The vertical segments of the coal seam are the benches, and from four to eight benches make up the sample set. Normally, the rock unit immediately overlying the coal also is sampled, as is the underclay (or other seat rock) and any rock parting within the seam over three-eighths of an inch thick. Each bench of coal is analyzed for the full range of chemical elements, and several of the associated rock units also have been extensively analyzed chemically. The data mentioned here are from the analyses of four such bench sets, and all the analyses were performed in the laboratories of the Illinois State Geological Survey (ISGS). With the cooperation of the United States Geological Survey (USGS), this work is being extended in scope and, in the future additional bench analyses will be made at both the ISGS and the USGS.

The four sets of bench samples recently analyzed at the ISGS are all from the Herrin (No. 6) Coal in Illinois.

Table 2. Summary of additional analytical values for 25 samples of Herrin (no. 6) coal from the Illinois basin (ppm)

Element	Arithmetic mean	Standard deviation	Range of values	
			Minimum	Maximum
Ag	0.19	0.24	< 0.03	0.80
Au	0.01	0.01	< 0.0004	0.032
Ba	130.	150.	33.	750.
Ce	11.	4.3	4.4	24.
Cs	1.0	0.26	0.49	1.5
Dy	0.99	0.30	0.70	1.81
Eu	0.23	0.07	0.10	0.40
Hf	0.45	0.14	0.24	0.81
I	2.0	1.2	< 1.0	5.8
In	0.02	0.02	< 0.008	0.09
La	6.9	2.2	3.3	12.
Lu	0.07	0.02	0.041	0.11
Rb	14.	4.0	7.4	20.
Sc	2.4	0.57	1.4	3.6
Sm	1.1	0.62	0.4	3.8
Sr	37.	20.	19.	130.
Ta	0.15	0.05	0.10	0.30
Tb	0.15	0.06	0.04	0.24
Th	2.01	0.47	1.2	3.3
U	1.6	1.1	0.5	4.5
W	0.74	0.56	0.04	2.1
Yb	0.51	0.13	0.31	0.77

The sample sites were selected to provide a range of geological and geochemical characteristics of the coals. Samples were taken from areas of high-sulfur coal and from areas of low-sulfur coal, from underground mines and from strip mines, and from areas with marine roof rocks and areas with nonmarine roof rocks. The four samples are separated geographically by as much as 70 miles, and no two sites are closer than 25 miles. In this discussion, the four sites will be identified by the letters J, M, P, and R.

As coal is a relatively heterogeneous material in all respects, wide variations in trace-element contents of individual benches are to be expected and, in general, that is what we are finding. However, we also find that in some bench sets, some elements occur uniformly throughout the seam. Perhaps the most uniform distribution observed thus far is that of bromine in sample set J (fig. 1). Figures 1-5 represent the benches of the total coal seam, with the proportional thickness of each bench plotted along the ordinate and the concentration of the element along the abscissa. The top of the coal seam, or the rock above the seam, is plotted at the top of each figure.

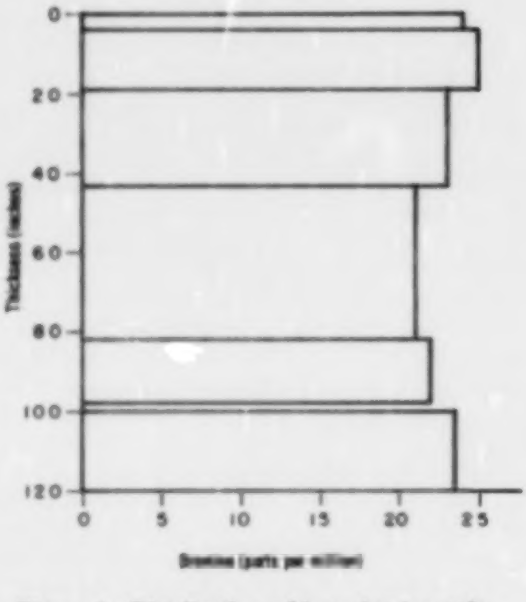


Figure 1. Distribution of bromine in coals of bench set J.

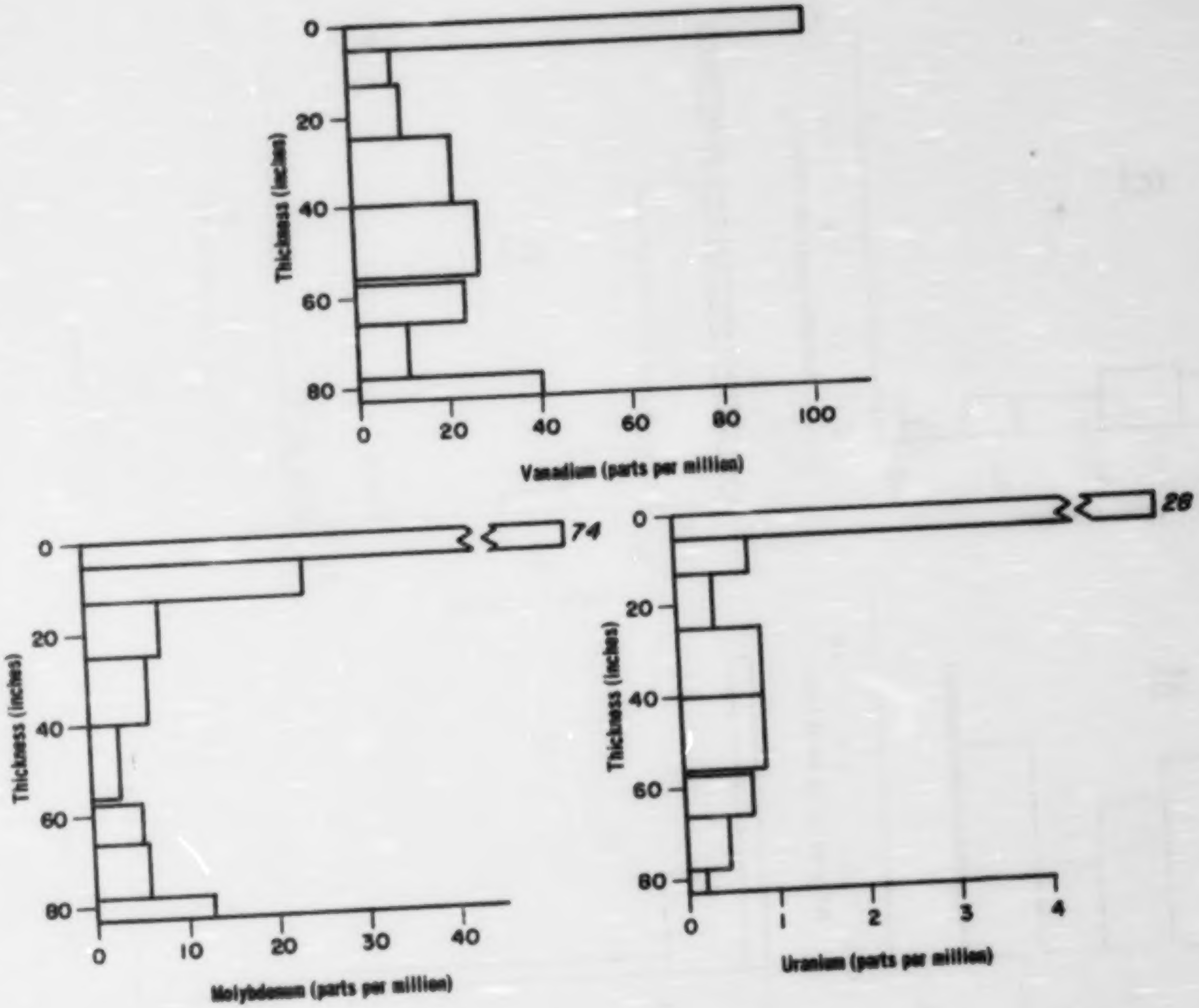


Figure 2. Distribution of vanadium, molybdenum, and uranium in coals of bench set R.

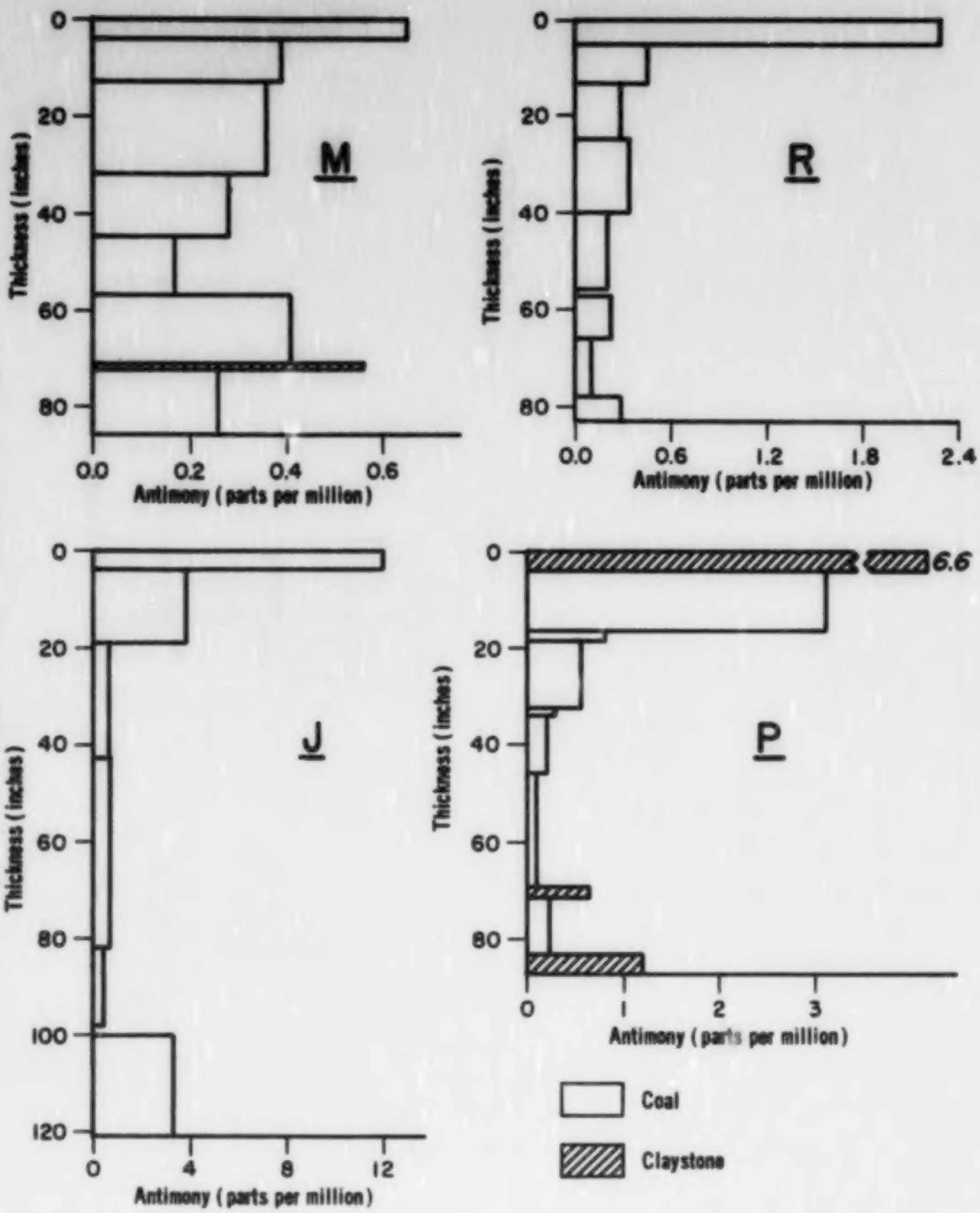


Figure 3. Distribution of antimony in coals of bench sets M, R, J, and P.

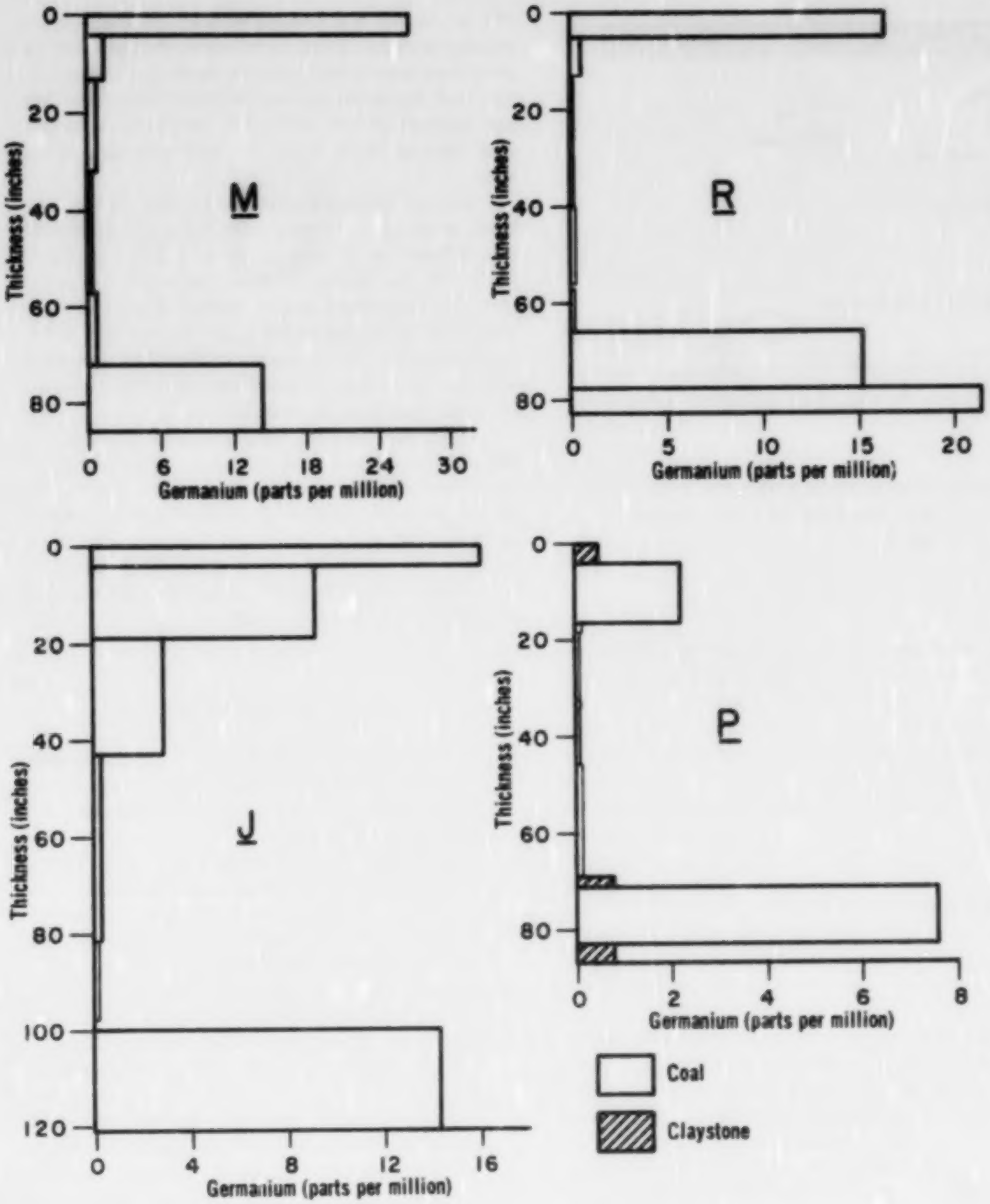


Figure 4. Distribution of germanium in coals of bench sets M, R, J, and P.

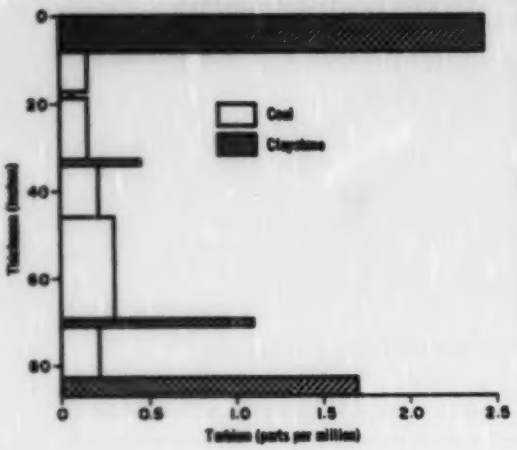


Figure 5. Concentration of terbium in coals and associated strata of bench set P.

The expected variability in trace-element distribution is apparent in figure 2. The three elements U, Mo, and V have a wide distribution range and in figure 2 are all concentrated in the uppermost bench of this sample set. Although we have not yet had the opportunity to determine statistically from the analytical data which part of the coal seam is most likely to contain concentrations of the trace elements, the top and/or bottom benches appear to be the most likely sites. The concentration of antimony in the uppermost bench of each of the four sample sets is represented in figure 3. The maximum concentration within the coal seam is in the top bench of each sample set, but even higher amounts of antimony were obtained from the rock units associated with the coals.

Distribution of germanium in the bench sets is shown in figure 4. The pattern is distinct and consistent in the four coals. The germanium content of the top bench and that of the bottom bench are both greater than the germanium content of any other bench in all four sample sets. Our earlier efforts, as well as those of Zubovic (ref. 5), demonstrated that germanium is primarily associated with the organic fraction of the coals in Illinois and not in the mineral matter fraction (refs. 3-5). This and the observation that the germanium is concentrated at the boundaries of the coal seam—the top and the bottom—suggest that the germanium was introduced into the coal seam after burial and is not related to conditions in the swamps in which the coal formed. The germanium was transported into the coal seam in solution and assimilated by the coal when geochemical conditions were favorable for the removal of the germanium from the solutions. The horizontal boundaries (top and bottom) of the seam were necessarily in contact with these solutions before the innermost parts of the seam.

The roof shale, underclay, and a clay parting (blue band) were analyzed along with the seven benches of coal in bench set P. Many elements, including Ba, Cs, F, Ga, Hf, In, La, Sc, Sr, Zr, and most of the rare earths that were determined, occur in higher concentrations in these rock units than in the coals. An example of the concentration of the elements in the strata associated with the coal is given in the illustration of terbium concentration (fig. 5) in bench set P.

All the data from the many analyses mentioned here will soon be published, the data analyzed statistically in detail, and the stratigraphic and geographic distribution of the elements mapped. These investigations should make available much information that will assist those who need to make informed decisions about the use of the energy resources of this country and about the environmental effects that may result.

REFERENCES

1. R. R. Ruch, H. J. Gluskoter, and E. Joyce Kennedy, "Mercury Content of Illinois Coals," Illinois State Geological Survey Environmental Geology Note 43, 15 p., February 1971.
2. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: An Interim Report," Illinois State Geological Survey Environmental Geology Note 61, April 1973.
3. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: A Final Report," Illinois State Geological Survey Environmental Geology Note 72, August 1974. Also distributed by U.S. Environmental Protection Agency publication 650/2-74-054, July 1974, NTIS TB 2308091/AS.
4. H. J. Gluskoter, "Mineral Matter and Trace Elements in Coal," *in* Babu, ed., *Trace Elements in Fuel*, Advances in Chemistry Series 141, American Chemical Society, 1975, pp. 1-22.
5. Peter Zubovic, "Physicochemical Properties of Certain Minor Elements as Controlling Factors in Their Distribution in Coal," *in Coal Science*, Advances in Chemistry Series 55, American Chemistry Society, 1966, pp. 221-230.

GEOCHEMISTRY OF TRACE ELEMENTS IN COAL

Peter Zubovic*

Abstract

The accumulation and distribution of inorganic elements in coal result from the interactions of geological, physico-chemical, and biochemical factors. Geological factors such as (1) rate of subsidence of a depositional basin; (2) rate of uplift of the drainage area; (3) types of rocks being eroded in the source area and deposited in a depositional basin; and (4) ratio of the size of drainage area to the area of organic accumulation, all determine the availability of the elements to the site of coal deposition.

Physico-chemical and biochemical factors control the accumulation and distribution of the elements at the site of organic deposition. Elements such as Ge, Be, and Ga have a high organic affinity, and are generally found in higher concentrations in coals deposited adjacent to source areas, whereas the transition metals are nearly uniformly distributed throughout a basin. Metals such as Zn, Cd, and Pb, when present in relatively high concentrations, have accumulated by post-depositional processes. The occasional high concentrations of these metals in coals appear to be related to known ore deposits. Some of the more toxic elements such as As, Hg, Se, and Sb do not appear to have a discernible distribution pattern in coals within a basin.

Generally, coals of the western states contain significantly lower concentrations of environmentally objectionable elements than do coals of the eastern or interior provinces.

INTRODUCTION

The introduction and retention of trace elements in coal results from a series of geologic and chemical processes. The end result of these processes is that many trace elements that are in low concentration and in a dispersed state in the parent rock are concentrated in coal. Further concentration and activation takes place when coals are utilized. Thus, trace elements eroded and transported from source areas of hundreds of thousands of square miles are entrapped in a much smaller volume of coal, which is then utilized at a point location. Organisms adapted to relatively low availability of trace elements in the general terrestrial environment may not be adapted to the environment produced when coal is utilized.

This paper is concerned primarily with the processes involved in the emplacement of the trace elements in coal. Because the coals of the Interior Province have been studied in greatest detail, most of the following discussion will focus on the geochemistry of the trace elements in these coals (fig. 1) (ref. 1). This discussion is, however, applicable to all coals.

GEOLOGICAL PROCESSES

The availability of any particular element to chemical emplacement processes in the coal-forming swamp is regulated by several geological processes in the source area. Rapid and extensive uplift of the source areas would tend to reduce the length of time necessary for chemical weathering and would result in a greater influx of clastic materials and a smaller amount of soluble inorganic matter into the depositional basin. Under these conditions, a larger amount of the trace elements would be associated with the nonauthigenic mineral matter of coal and a lesser amount with the organic fraction.

Tectonic and climatic activity in the depositional basin must maintain conditions for the accumulation of organic matter. If subsidence is too rapid, little or no vegetation will be able to grow and clastic materials will dominate the depositional sequence. If little or no subsidence takes place, the biochemical cycle will be essentially completed, and most of the vegetative organic matter will be oxidized. For organic matter to accumulate in significant quantities, an optimum balance of tectonic and climatic conditions must exist.

The rate of accumulation of organic matter is important in determining the concentration of trace elements in the resulting coal. If the availability of trace elements from a source area remains constant, then the concentrations that will result in the organic matter will be inversely proportional to the rate of accumulation of the organic matter.

In addition, if the areal extent of organic deposition is large, then low concentrations of trace elements will result. This is why generally thick widespread coal beds have low trace-element concentrations and, conversely, why thin-bedded coals have high concentrations.

During the initial phase of organic accumulation in a basin, the trace elements may be obtained by the plants from the underlying soil profile. When the peat accumulates to a point where the root systems are within the peat, then the dominant source becomes the elemental

---

*The author is with the U. S. Geological Survey, Reston, Virginia 22092.

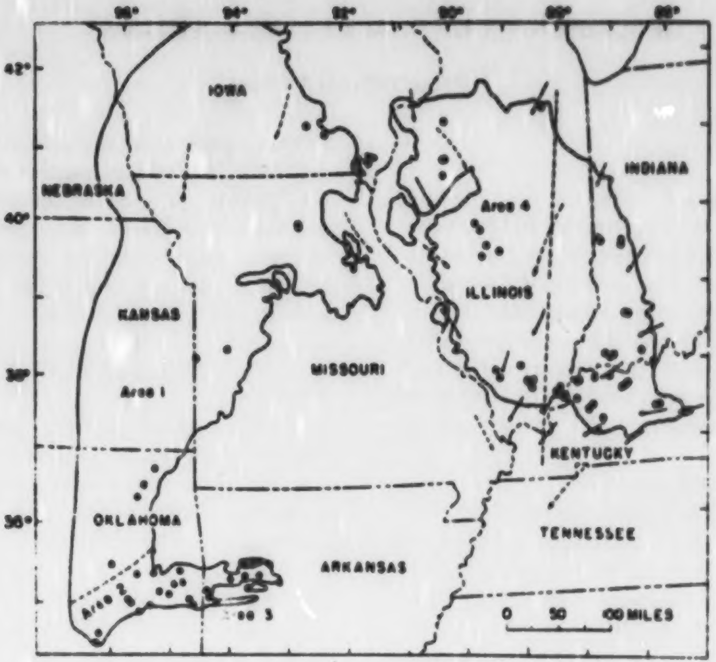


Figure 1. Distribution of coal samples in the Interior Province. Solid line indicates extent of Pennsylvanian sedimentary rocks containing coal beds; arrows indicate transport directions of sediments that become basal Pennsylvanian sandstones. Samples east of dashed line in Eastern region not used in plots (ref. 1).

influx from the surrounding borderland. The mineral matter that makes up the soil must probably also had its origin in the same area.

Zubovic et al. showed (ref. 2) that the trace-element content of coal can be related to the type of rocks being eroded. Potter and Glass reported (ref. 3) that during Pennsylvanian time, rocks of the source area contributing sediments to the Illinois basin progressively changed from recycled sediments to more immature types, including some contributions from metamorphic and igneous rocks. Igneous rocks, particularly the mafic types, are the principal original source of the dark minerals that contain most of the V, Cr, Co, Ni, and Cu in these rocks. The dark minerals (amphiboles, pyroxenes, sulfides) are less resistant to weathering and to abrasion during transport than are the light-colored minerals, such as quartz and feldspar. As a result, the metals that make up these dark minerals have a higher seaward-migration rate than those found in the more resistant minerals. Consequently, most recycled sediments would be depleted in metals such as mentioned above. As a result of these geologic conditions, progressively larger amounts of these metals should be available to the younger Pennsylvanian coals. According to the data, this appears to be the case.

In some coals of the Interior Province, high concentrations of zinc (>500 ppm) are frequently found. When zinc is present in high enough concentrations, the mineral sphalerite (ZnS) has been identified (refs. 4 and 5) as fracture fillings in the coal. It appears that all the Cd found in coal is associated with the sphalerite (ref. 5). As the sphalerite is deposited in fractures, most of it is removed from the coal when the coal is crushed and washed. Obviously, the cadmium associated with the zinc in sphalerite is also removed. Highest concentrations of zinc are found in areas of the coal basin nearest known areas of zinc mineralization such as the upper Mississippi Valley District of Illinois and Wisconsin, the Tristate District, and the Southern Illinois District. Coals in the intermediate areas have far lower zinc contents.

At present, the reason for this difference has not been definitely established.

Heyl et al. (ref. 6) suggested that mineralization of the Wisconsin and northern Illinois lead-zinc ores took place between late Paleozoic time and the close of Mesozoic time. As the coals in these areas were deposited in late Paleozoic time (Pennsylvanian), the processes that introduced the lead and zinc into the carbonates and other sediments of northern Illinois and Wisconsin may also have introduced these elements into the coals of the Interior Region.

These minerals were deposited in fractures; therefore, the coal must have undergone considerable diagenetic transformation past the peat stage to be hard enough for fractures to have formed. The mineralization is probably post-Paleozoic. If the zinc had been introduced into the coals during Mesozoic time, it could still have been obtained from the same source as the ore deposits north of the coal basin. If, however, the zinc enrichment of coal was post-Mesozoic, then weathering and erosion of the existing ore deposits could have been the source of zinc in the coal.

Physico-Chemical Processes of Trace-Element Emplacement in Coal

Interactions of elements with sulfide ions and organic ligands.

Trace elements in solution entering an area in which organic matter is being deposited are subjected to retention according to the principles of coordination chemistry. It can be assumed that a large variety of organic ligands is present within such an organic environment. This environment would also be conducive to the growth of sulfate-reducing bacteria and consequently to the production of H_2S, which dissociates into HS^- and $S^=$. There would then be competition between the organic ligands and sulfide ions for the available metal ions, particularly the chalcophilic elements such as Cu, Pb, Zn, Cd, Sb, Hg, and Fe.

The partition of these elements between sulfide and organic phases is dependent upon the concentration of organic ligands and of the sulfide ions. Because this is a dominantly organic environment, the concentration of organic ligands would remain relatively uniform. The concentration of sulfide ions could vary considerably, as their availability is dependent upon the influx of sulfate ions as well as upon the development of sulfate-reducing bacterial colonies which would produce H_2S. That the availability of sulfide ions is erratic is best indicated by the sporadic occurrence of sulfide in coal. Frequently, massive pyrite is found adjacent to coal that is free of this mineral. When the sulfide ions are uniformly available, then small disseminated crystals of pyrite are found throughout the coal.

In addition to a discussion of the availability of the reacting anionic species, consideration must be given to the stability of the compounds that could be formed. This stability can be compared by considering the dissociation constant of the compounds. Because however, no data are available on the dissociation constants of metallo-organic compounds in a swamp environment, consideration must be theoretical and based on concentrations of the dissociated metal ions. If the concentration of the dissociated metal ion is lower in the presence of the sulfide of the metal than it is for any possible metallo-organic compound it could form, the reaction would be directed toward the formation of sulfides. Conversely, if it is higher, then metallo-organic complexes would be formed. A hypothetical phase diagram of such conditions is shown as fig. 2. No units are indicated. However, the relations are applicable to any units which are comparable. An illustration of such competitive reactions is shown by the reaction of copper-amino acid complexes with H_2S. When H_2S is added to a solution of the copper complex, CuS is precipitated. Equilibrium constants for the copper amino acid complexes are about 10^{-17}, whereas that for CuS is about 10^{-44}. Obviously, if H_2S is present, CuS will form. The fact that copper has some organic association in coal is an indication of the absence of any sulfate-reducing activity at the time organically associated copper was introduced into that particular area of the swamp. The preceding discussion is applicable to all the chalcophilic elements.

Determination of Organic Association of Metals in Coal.

The suggestion that organic complexes of various metals exist in coal and other organic sediments is based on indirect evidence. With the exception of V and Ni porphyrins, no other organic complex has ever been isolated or identified in organic sediments. The suggestions by many investigators that metallo-organic complexes exist in coal is based on observations that elements such as Ge and Be were always found in large amounts in the ash of clean coal and ash of pure coal macerals such as vitrinite.

The first attempt to quantify the organic association of metals in coal was made by Horton and Aubrey (ref. 7). Three vitrain samples were separated by sink-float techniques, and the quantities of each element contained in the different specific gravity fractions were determined. In their samples, Ge and V were 100 percent associated with the organic fraction, whereas Sn was 100 percent associated with the mineral fraction of coal. The other elements had intermediate associations (table 1).

Zubovic (ref. 8), in a study of 13 coal samples, in which he used sink-float methods, reported a dominant

Table 1. Average organic affinity of some metals determined by float-sink methods

[N.D., not determined]

Element	Percent organic affinity (ref. 8)	Percent organic association (ref. 7)
Germanium	87	100
Beryllium	82	75 – 100
Gallium	79	75 – 100
Titanium	78	75 – 100
Boron	77	75 – 100
Vanadium	76	100
Nickel	59	0 – 75
Chromium	55	0 – 100
Cobalt	53	25 – 50
Yttrium	53	N.D.
Molybdenum	40	50 – 75
Copper	34	25 – 50
Tin	27	0
Lanthanum	3	N.D.
Zinc	0	50

organic association for the same six elements reported in ref. 7 as having a high organic association. In this study, zinc showed no organic association (fig. 3). Ruch et al. (ref. 9) reported on the organic association of 21 elements in four coal samples. Ge, Be, and B were found to be organically associated, whereas Hg, Zr, Zn, Cd, As, Pb, Mo, and Mn were largely associated with the mineral matter of the coal. The other elements had varying degrees of organic association. The Ruch et al. studies were based on a physical separation of the organic fractions from the mineral matter of coal and on an investigation of the distribution of the elements in these components. The studies indicate that most of the elements have a partial organic and partial inorganic association. Some of the inorganic associations, especially for the chalcophilic elements are caused by the formation of sulfides, as previously discussed. Some of the inorganic associations shown by such elements as Ge, Be, B, Zr, and others result from their introduction into the coal-forming swamp in resistant clastic minerals.

Additional evidence for the existence of organic complexes (chelates) for some of the elements in coals is shown by the relation of the organic affinity of the elements in coal to the complexing ability of these metals with organic ligands. The stability of chelates of the metals is directly related to the ionic potential of these elements. The organic affinity of the metals in coal is also related to their ionic potential (fig. 3). This suggests that those metals having high organic affinity in coal are present as chelates.

Compilations of stability constants for a wide range of organic ligands (ref. 10) give a stability order of Ga>Y>La for these trivalent metals. This is the same order as is their organic affinity (fig. 3). Other compilations for the bivalent metals (refs. 10,11) suggest that their stability order is Be>Cu>Ni>Co>Zn>Fe. In coal, the organic affinity for some of these elements is Be>Ni>Co>Co>Cu>Zn. Iron, of course, is always dominantly present as the sulfide. With the exception of copper, the two series are identical. The displacement of

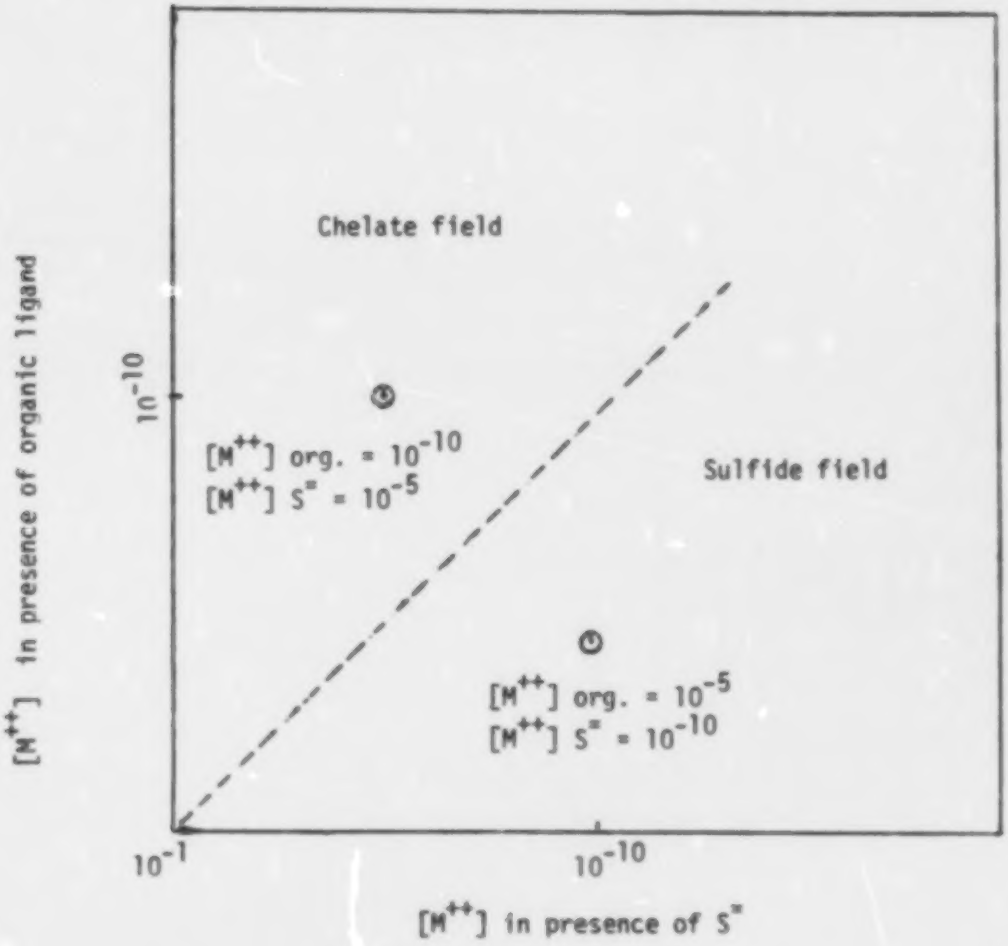


Figure 2. Hypothetical phase diagram showing relation of the dissociation of divalent chalcophilic metals to their sulfide and chelate phases.

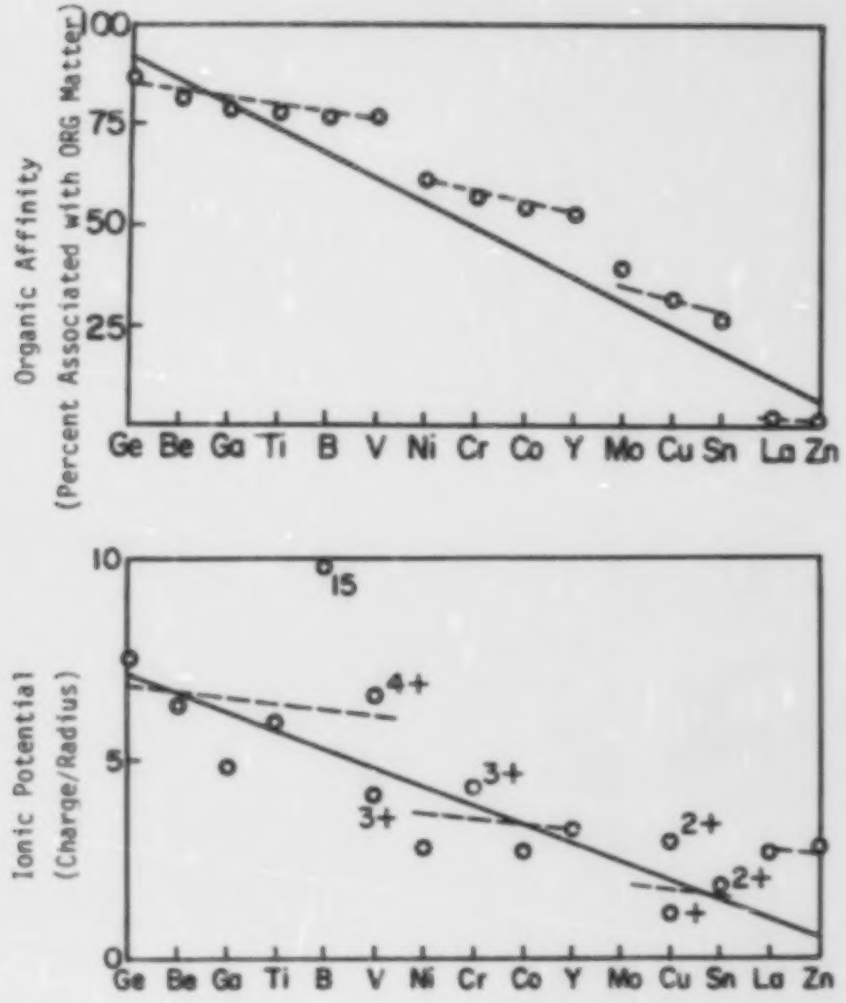


Figure 3. Relation of organic affinity and ionic potential of the elements arranged in order of decreasing affinity for organic matter.

copper to a lower organic affinity than is indicated by its stability series results from its occasional interaction with sulfide ions, as discussed previously. The evidence indicates that metals that have high organic affinity in coal are present as chelates.

Breger et al. (ref. 12) made an intensive study of the forms of uranium in a North Dakota lignite. By using ion exchange and acid leaching of the lignite, they determined that more than 85 percent of the uranium was bound as an metallo-organic compound and the 1.2 percent was held in ion-exchange positions. The rest was assumed to be inorganically associated.

Trace-Element Distributions in a Coal Basin.

The geographic distribution of the elements in a coal basin appears to be controlled by their chemical properties. In the following figures (figs. 4-8), the coal samples are arranged to portray a cross section of a basin. Samples nearest to the edges of the diagrams are closest to the northern margins of the basin and thus to the source areas. Samples in the center columns are farthest from the source area. Location of the samples is shown in fig. 1.

Elements possessing a high organic affinity, such as Ge, Be, B, and Ga have high concentrations in the near-source areas and elemental depletions in distal areas (figs. 4,5) (ref. 1). Antimony, which Gluskoter (ref. 5) reported as having a high organic affinity, has similar distribution patterns. The transition metals, which have a lower organic affinity, are uniformly distributed throughout the basin (figs. 6,7). Most of the chalcophilic elements behave in the same manner. The diagrams also show that the elements having lower organic affinities have a greater seaward migration than do those with higher organic affinities, as was suggested earlier.

The Y and La distribution in the coals of the basin provides a unique diagnostic display of the effect of their differing organic affinities. The data plots (fig. 8) indicate little if any differences in their distribution.

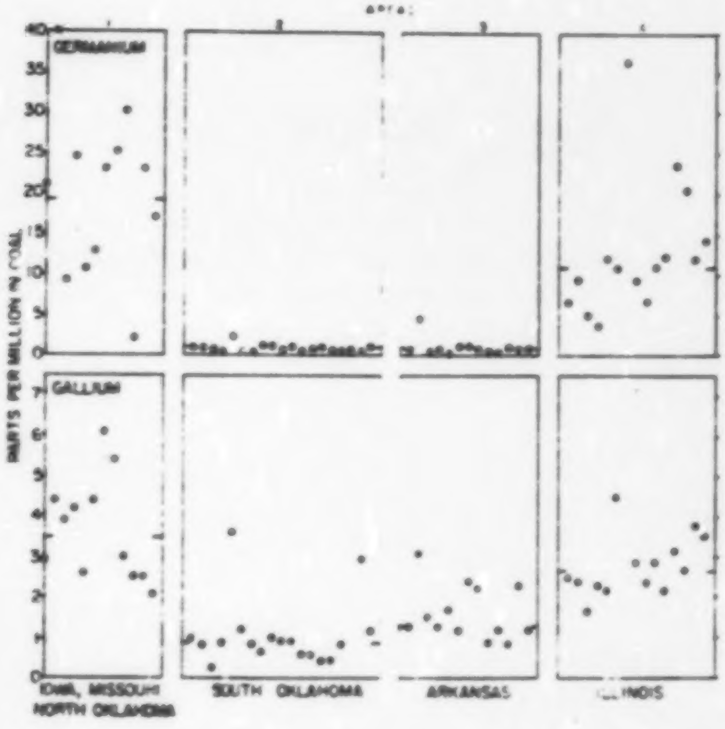


Figure 4. Distribution of germanium and gallium. Tick marks indicate medians for the elements in the samples. Areas 1 and 4 are near elemental source area (ref. 1).

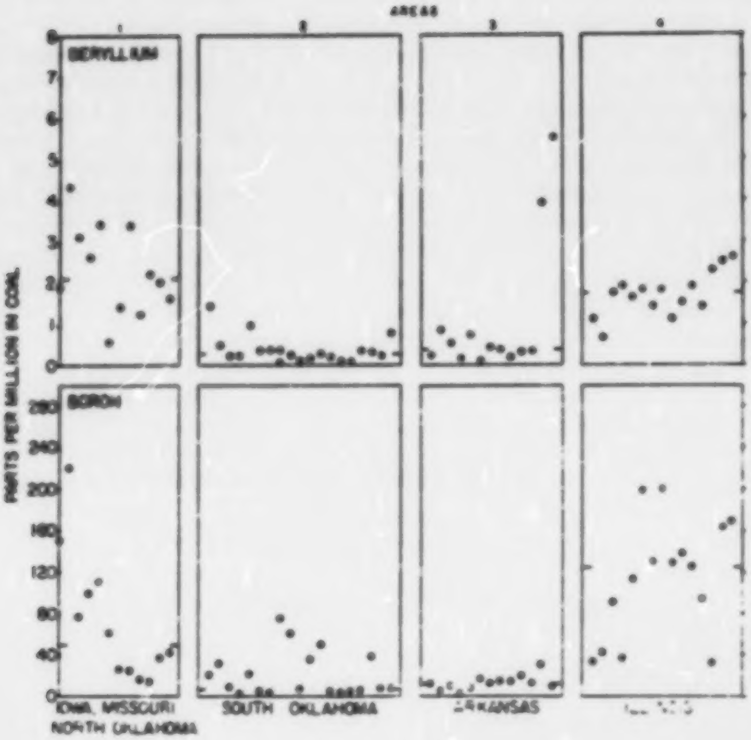


Figure 5. Distribution of beryllium and boron. Tick marks indicate medians for the elements in the samples. Areas 1 and 4 are near elemental source area (ref. 1).

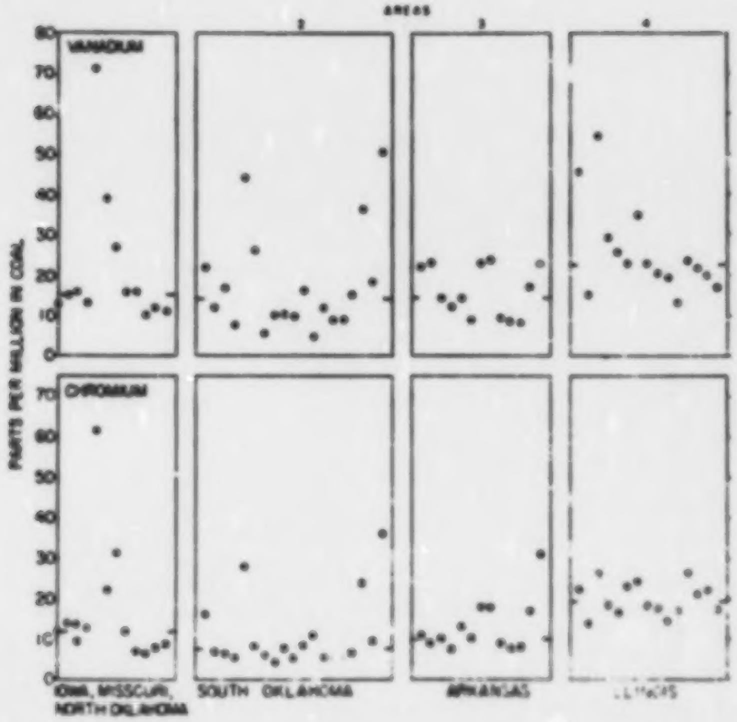


Figure 6. Distribution of vanadium and chromium. Tick marks indicate medians for the elements in the samples. Areas 1 and 4 are near elemental source area (ref. 1).

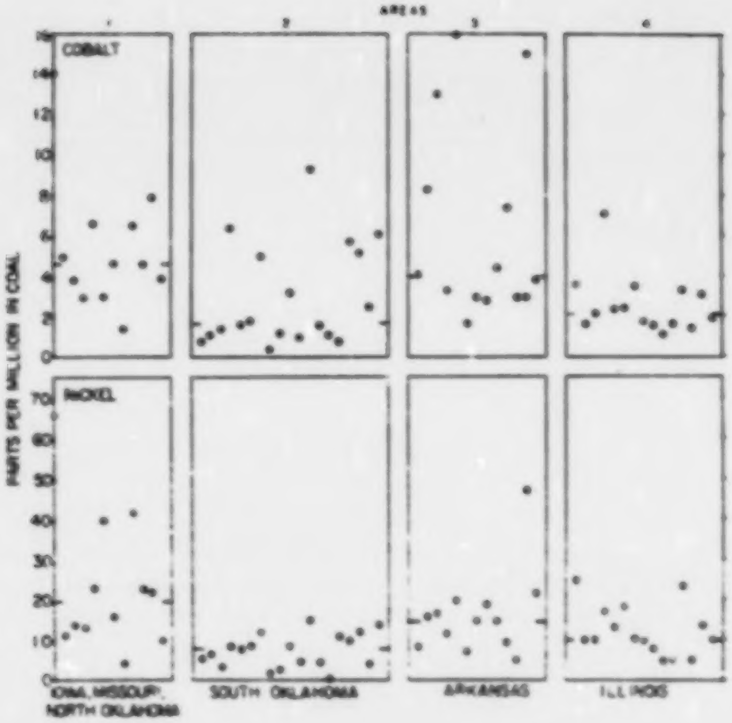


Figure 7. Distribution of cobalt and nickel. Tick marks indicate medians for the elements in the samples. Areas 1 and 4 are near elemental source area (ref. 1).

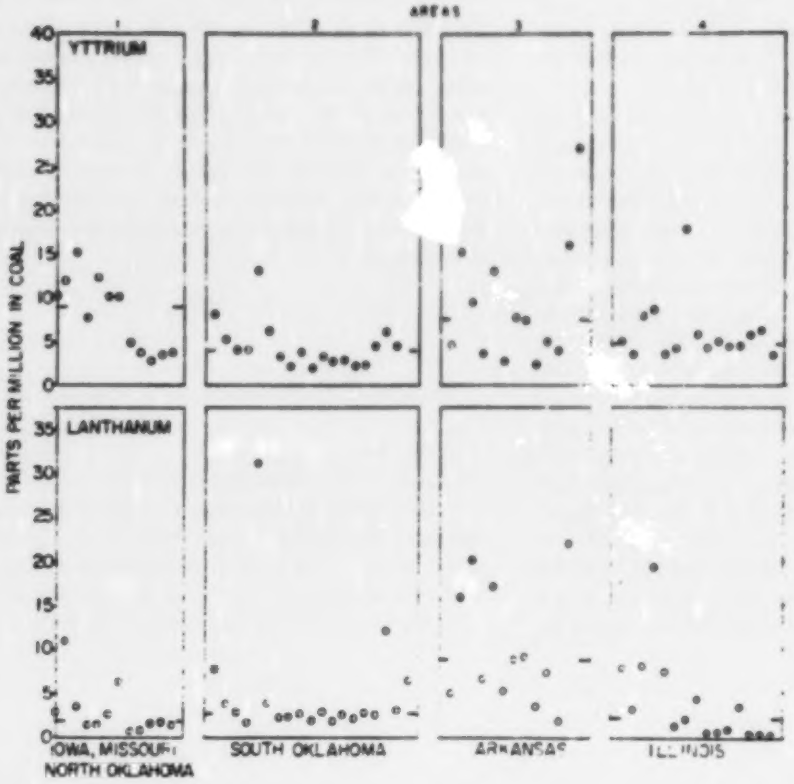


Figure 8. Distribution of yttrium and lanthanum. Tick marks indicate medians for the elements in the samples. Areas 1 and 4 are near elemental source area (ref. 1).

However, when the Y/La ratios are plotted (fig. 9), a significant separation of these elements takes place. Yttrium, which has a higher organic affinity than La, is significantly more enriched over La in the near-source areas. Thus, the behavior of Y resembles that of the other elements that have high organic affinities.

Vertical distributions of the elements also have significant regional differences. The three samples from Illinois bed 5 in figs. 10, 11, and 12 were collected at the northern, central, and the southern parts, respectively, of the coal basin. As the distance from the source area increases, the elemental distribution patterns (except for boron) become very similar. A pattern closely resembling that of the ash is evident. The heterogeneity of the element distribution in the near-source sample (fig. 10) can be explained by the fact that many of the elements may be entering the swamp area as undissolved clastic minerals. In addition, those elements in solution would not be subjected to entrapment processes before entering the area of organic deposition. This explanation also holds for coals deposited adjacent to the distributory channels within the swamp. The solutions reaching the deeper recesses of the swamp become depleted in soluble elements. The elemental concentrations in these waters assume relations to each other which are dependent upon the dissociation constants of the most stable compounds that could be formed in the marginal areas of the swamp. Additional complexing or other reactions can take place only if the equilibrium concentrations are exceeded. This can take place only by evaporation of water, which would result in a uniform concentration increase for all the elements and give the type of distributions depicted in figs. 11 and 12. The degree of variance found vertically throughout the bed is caused by changes in the residence time of the solutions in the swamp, which, in turn, is largely dependent upon climatic conditions.

REGIONAL DISTRIBUTION OF THE ELEMENTS

The average trace-element contents of coal from four areas in the United States are listed in table 2.

The Eastern Interior region is highest in six of these elements, the Northern Great Plains, in five, the Appalachian region, in three, and Western Interior region, in one. The distribution of environmentally objectionable elements in coals is shown in table 3 (refs. 9,13).

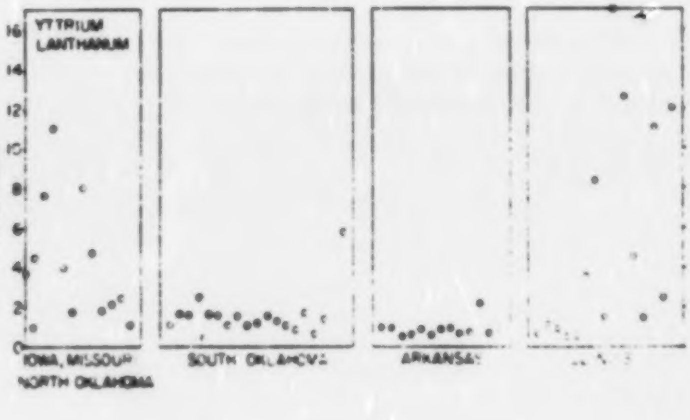
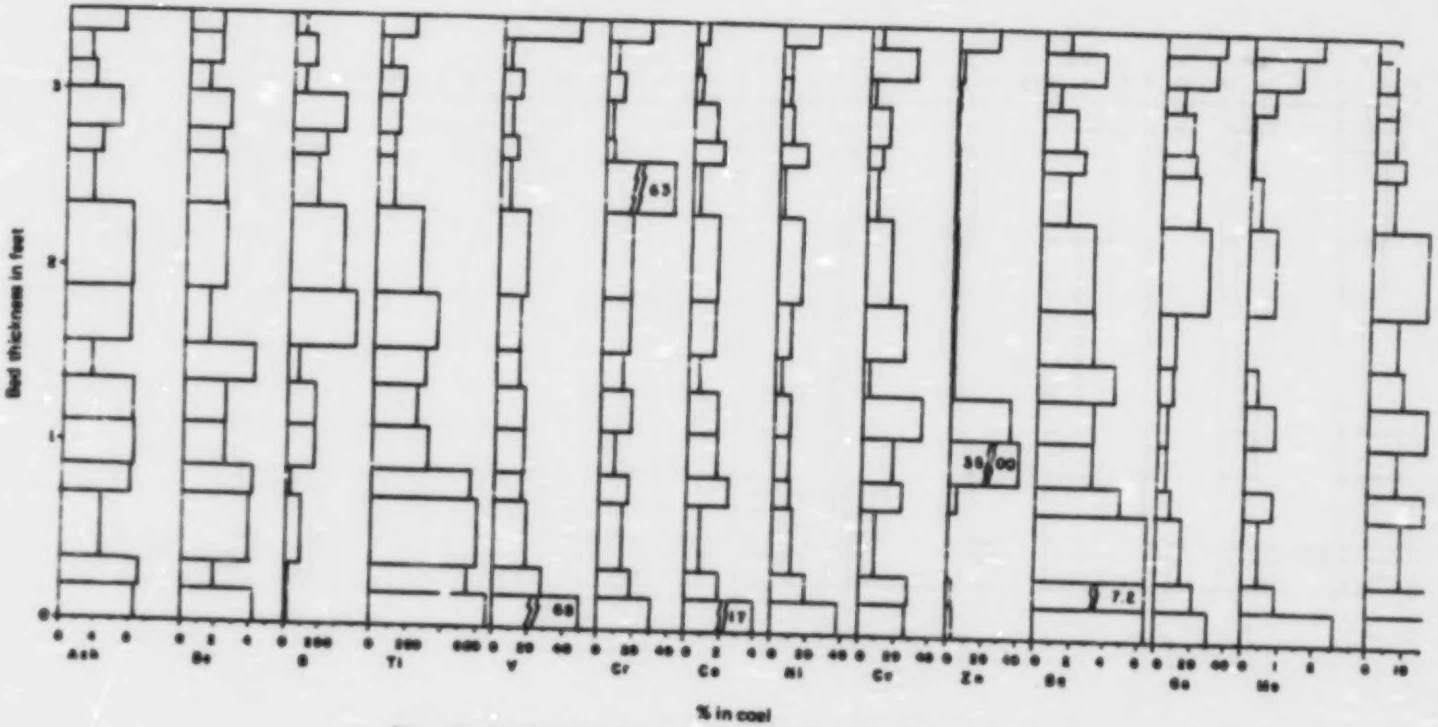
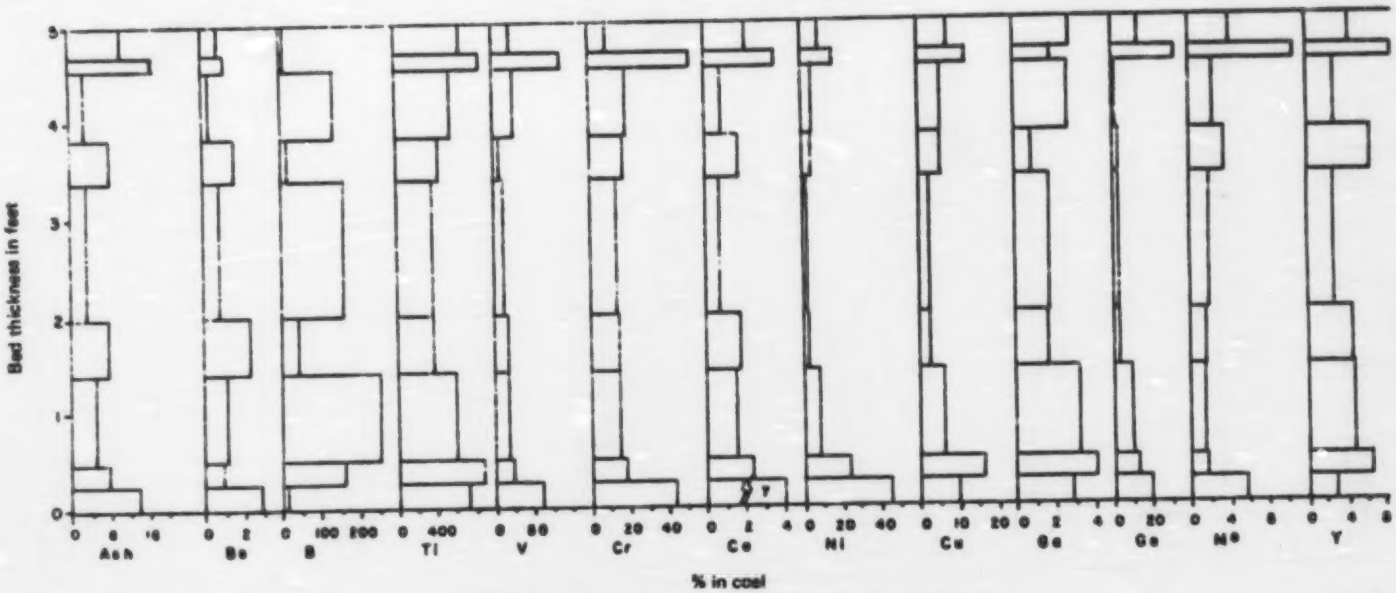


Figure 9. Distribution of the yttrium/lanthanum ratios. Areas 1 and 4 are near elemental source area (ref. 1).



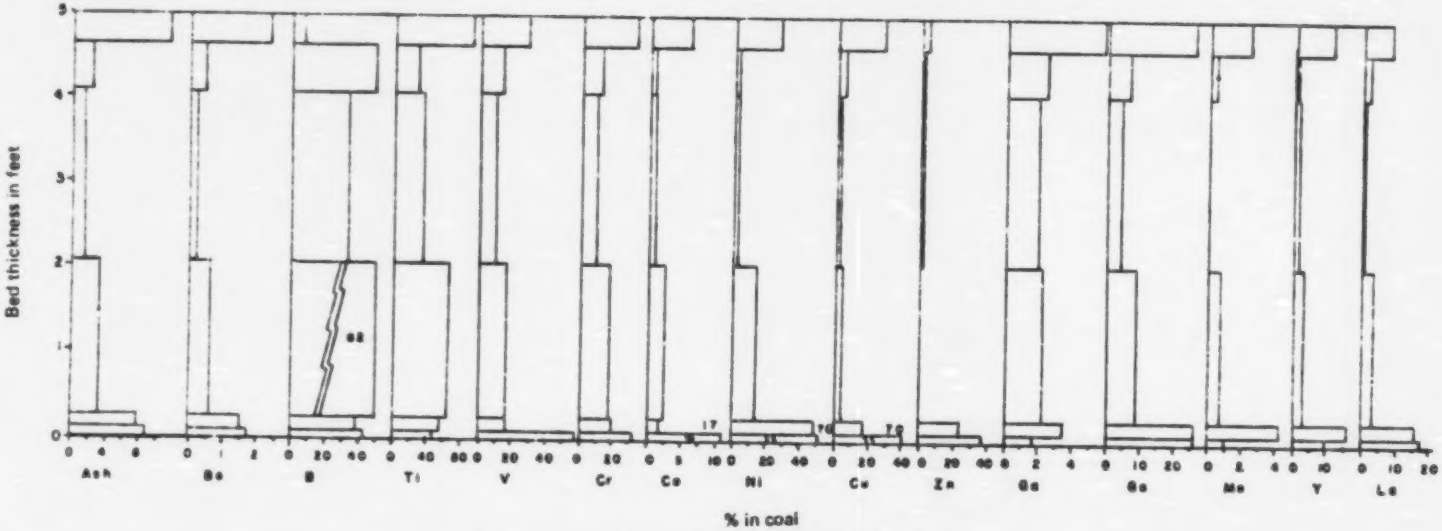
Note: Numbers for the elements are parts per million in coal; ash is percent in coal.

Figure 10. Vertical distribution of the elements in sample I11-E-5, taken from the northern edge of the coal basin near the elemental source area.



Note: Numbers for the elements are parts per million in coal.

Figure 11. Distribution of the elements in sample I11-F-5, taken from the central part of the coal basin, some distance from the elemental source area.



Note: Figures for the elements are parts per million in coal.

Figure 12. Vertical distribution of the elements in sample I11-H-5, taken from the southern part of the coal basin, farthest from the elemental source area.

Table 2. Trace-element content of American coals

[Parts per million]

Element	Northern Great Plains	Western Interior region	Eastern Interior region	Appalachian region
Be	1.5	1.1	2.5	2.5
B	116	33	96	25
Ti	591	250	450	340
V	16	18	35	21
Cr	7	13	20	13
Co	2.7	4.6	3.8	5.1
Ni	7.2	14	15	14
Cu	15	11	11	15
Zn	59	108	44	7.6
Ga	5.5	2.0	4.1	4.9
Ge	1.6	5.9	13	5.8
Mo	1.7	3.1	4.3	3.5
Sn	.9	1.3	1.5	.4
Y	13	7.4	7.7	14
La	9.5	6.5	5.1	9.4

Table 3. Distribution of environmentally hazardous trace elements

[Parts per million in coal]

Element	Powder River Basin	Western Interior region	Eastern Interior region	Appalachian region
Sb	0.67	3.5	1.3	1.2
As	3	16	14	18
Be	.7	2	1.8	2.0
Cd	2.1	20	2.3	.2
Hg	.1	.13	.19	.16
Pb	7.2	–	34	12
Se	.73	5.7	2.6	5.1
Zn	33	–	250	13

The highest concentrations of Sb, As, Be, Cd, and Se occur in the Western Interior region. Hg, Pb, and Zn are highest in the Eastern Interior region. Be is high in the Appalachian region, whereas Powder River Basin coals are lowest in all three elements.

SUMMARY

Geological factors are principally responsible for the availability of trace elements to the emplacement processes of a coal-forming swamp. These same factors are responsible for regional differences in the trace-element content of coals. Physicochemical processes control the type of associations that various metals will have in coal as well as their distribution in the coal of a basin.

Some of the trace-element distributions, such as the concentrations of elements having high organic affinities and the vertical similarity or heterogeneity of the elements within a bed, can be used to ascertain the position of the coal within the depositional basin. It can also be used to predict the type of distribution that will be found in the vicinity of the sampled area.

REFERENCES

1. Peter Zubovic, "Minor Element Distribution in Coal Samples of the Interior Coal Province," Advances in Chemistry Series 55: 231-247, 1966.
2. Peter Zubovic, T. M. Stadnichenko and Nola B. Sheffey, "Relation of the Minor Element Content of Coal to Possible Source Rocks,' U. S. Geological Survey Prof. Paper 400-B: p. 683, 1960.
3. P. E. Potter, and H. D. Glass, "Petrology and Sedimentation of the Pennsylvanian Sediments in Southern Illinois," Illinois State Geological Survey Report of Inv. No. 24: 52-53, 1958.
4. Peter Zubovic, "Minor Element Content of Coal from Illinois Beds 5 and 6 and their Correlatives in Indiana and Western Kentucky," U. S. Geological Survey, open-file report; 79 pp., 1960.
5. H. J. Gluskoter, and Peter C. Lindahl, Cadmium: Mode of "Occurrence in Illinois Coal," *Science, 181*: 264-266, July 20, 1973.
6. Allen V. Heyl, Allen F. Agnew, Erwin J. Lyons, and Charles H. Behre, Jr., "Geology of the Upper Mississippi Valley Zinc-Lead Deposits," U. S. Geological Survey Prof. Paper 309, 1959.
7. L. Horton and K. V. Aubrey, "The Distribution of Minor Elements in Vitrain: Three Vitrains from the Barnsley Seam," J. Soc. Chem. Industry, 50 (suppl. issue 1): 541-548, London, 1950.
8. Peter Zubovic, "Physicochemical Properties of Certain Minor Elements as Controlling Factors of their Distribution in Coal,' Advances in Chemistry Ser. 55: 221-230, 1966.
9. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," Illinois State Geological Survey, Environ. Geol. Note 72: 96 p., 1974.
10. F. Basalo, and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958.
11. H. Irving, and H. Rossotti, *Acta Chem. Scand., 10*, No. 1: 72-93.
12. Irving A. Breger, Maurice Deul, and Samuel Rubenstein, "Geochemistry and Mineralogy of a Uraniferous Lignite," *Econ. Geol., 50(2)*: 206-226, 1955.
13. Jack Medlin, Personal Communication, U. S. Geol. Survey.

Session II:

PROCESS TECHNOLOGY

E. C. Cavanaugh
Session Chairman

Preceding page blank

TRACE ELEMENTS AND MAJOR COMPONENT BALANCES AROUND THE SYNTHANE PDU GASIFIER

A. J. Forney, W. P. Haynes, S. J. Gasior,
R. M. Kornosky, C. E. Schmidt, and A. G. Sharkey*

Abstract

A series of gasification tests were run in the SYNTHANE PDU gasifier in an attempt to define the distribution in the effluent streams of the trace elements that enter the gasifier in the coal. The feed coal and nongaseous products were analyzed for 65 trace elements. Results indicate most of the elements are found in the char and dusts with some specifically in the tars and waters. More accurate methods of analysis are needed to make reasonable balances of the trace elements.

INTRODUCTION

Many coal-to-gas plants are expected to be constructed in the United States in the 1980's to supplement the dwindling supplies of gas. Because of environmental considerations, it is important to know the fate of various trace elements fed into the gasifier in the coal during coal gasification. This report is a first attempt to analyze all feed and product streams of the small SYNTHANE laboratory gasifier. This gasifier has the advantage that all feed and effluent streams are representative of those that will be obtained from a commercial operation. In these experiments, only one coal—Illinois #6 (River King Mine, Monroe Co., Illinois) was used since it is believed that the Illinois coals, (because of their high sulfur content and enormous reserves) are the prime candidates to be used in the first commercial coal-to-gas plants east of the Mississippi.

Other authors have discussed trace elements, (refs. 1,2) but this we believe is a first attempt to make balances of trace elements around the gasifier.

THE GASIFIER

A schematic diagram of the laboratory gasifier is shown in figure 1. The gasification section is a 6-foot long section of 4-inch diameter pipe (310 SS) inside a 10-inch pipe (304 SS) acting as a pressure shell, with heaters and refractories in the annulus. Above the gasification section is another 6-foot section of 10-inch diameter pipe. The 4-inch section contains the high (1832° F) temperature fluid bed. Coal, steam, and oxygen are the feeds to the gasifier (plus some nitrogen) and the products are the char, filter fines, tar, water, and gas. With a mildly caking coal like Illinois #6, it was necessary to pretreat the coal. While commercially the pretreating feed gases would be steam plus oxygen, in the small unit, nitrogen plus oxygen is used to avoid problems due to steam condensation. The products from the pretreater enter the gasifier so there are no separate byproducts. Other analyses from the gasifier are discussed in more detail in an earlier publication (ref. 3).

THE TESTS

A series of gasification tests were made in the gasifier using Illinois #6 coal. Attempts were made to hold conditions as constant as possible. The overall results of 3 of the tests are shown in table 1. In addition to the regular analysis made on the feed coal and the product streams, trace element analyses were made on the coal feed, the feed water and the char, fines, tar, water, and gases. The trace element analysis was done by spark source mass spectrometric analysis (SSMS) on all except the gas. Trace elements in the gas were determined by neutron activation, but results were incomplete and not conclusive. Determinations on the feed water were also incomplete. Mercury analysis was done by flameless atomic absorption procedures.

Samples were taken as follows:

1. Solids are collected from hoppers by a vacuum connected to a cyclone separator tank. Samples are then taken by randomly scooping some coal or char out with the sample can.
2. Condensate and tar mixture is drained from the condenser into 5-gallon steel buckets, decanted and individual tar and condensate samples are taken randomly by dipping glass jars into the buckets of decanted condensate and tar.

There were 3 separate sets of data obtained for each separate test, # 162, 163, and 164.

---

*The authors are with the Energy Research and Development Administration, Pittsburgh Energy Research Center, Pittsburgh, Pennsylvania. Forney is a research supervisor; Haynes and Gasior are supervisory chemical engineers; Kornosky, a chemical engineer; Schmidt, a research chemist; and Sharkey, a supervisory research physicist.

Preceding page blank

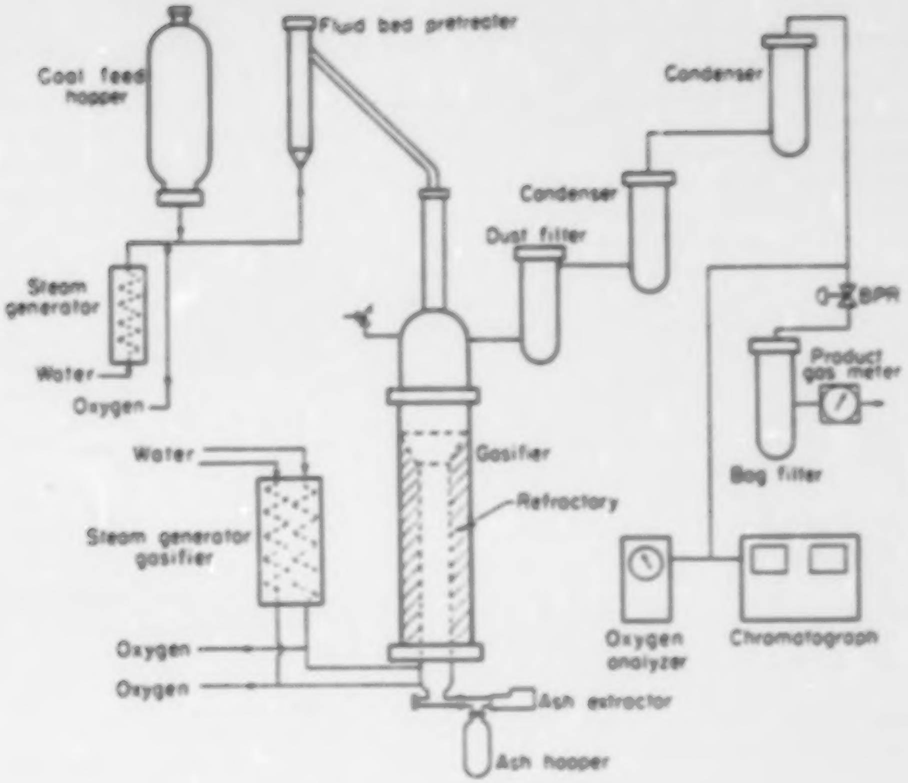

Coal feed hopper
Fluid bed pretreater
Condenser
Condenser
Dust filter
Steam generator
Water
Oxygen
BPR
Product gas meter
Gasifier
Refractory
Bag filter
Water
Steam generator gasifier
Oxygen analyzer
Chromatograph
Oxygen
Oxygen
Ash extractor
Ash hopper

Figure 1. Bruceton 40-atmosphere gasifier.

Table 1. Run conditions and results for all tests

Run Conditions	162	163	164
Time (Hrs)	6.25	5.50	6.67
Coal Feed Rate #/hr.	20.0	20.4	23.7
Coal Feed #/hr-ft^3	42.6	43.3	50.4
#Steam/#Coal Feed	1.68	1.75	1.54
#O_2/#Coal Feed	0.37	0.37	0.30
Pressure (ATM)	40	40	40
Temperature Pretreater, °C			
Max.	408	409	406
Avg.	363	364	349
Temperature Gasifier, °C			
Max.	985	1020	990
Avg.	917	918	925
Gasifier Sup. L. Vel. (ft/sec)	0.29	0.30	0.29
Pretreater Sup. L. Vel. (ft/sec)	0.79	0.80	0.71
Run Results			
SCF Prod[1] Gas/#Coal	12.3	12.6	11.7
SCF CH_4 Eq/#Coal	3.08	3.01	3.15
Steam Decomp, %	17.8	17.6	19.0
Carbon Gasified, %	67.1	68.5	66.5
Carbon Converted, %	71.4	72.2	71.7
#Tar/#Coal Feed	0.03	0.02	0.04
CH_4 (EQU) % of Purified Gas	24.6	23.4	26.3
Gas Analysis, Dry, N_2 Free (%)			
H_2	35.1	35.7	35.4
O_2	0.0	0.0	0.0
CO	12.0	13.3	12.3
CH_4	12.8	12.4	13.9
CO_2	37.4	35.8	35.3
C_2H_6	1.29	1.30	1.56
H_2S	1.43	1.41	1.62

[1] $H_2 + CO + CH_4 + C_2H_6$

Gas Analysis, Dry, N_2 Free (%)			
CH_3SH	0.002	0.002	0.003
COS	0.014	0.020	0.030
SO_2	0.001	0.001	0.001
C_4H_4S	0.004	0.001	0.004
C_6H_8S	0.001	0.001	0.001
C_6H_6	0.039	0.012	0.022
C_7H_8	0.010	0.003	0.005
C_8H_{10}	0.002	0.002	0.002
HCN	8.8×10^{-9}	3.2×10^{-8}	9.1×10^{-9}
C_5H_6S	0.001	0.001	0.001

Table 2. Feed stream into the gasifier
(tests 162, 163, 164)

	162	163	164
Coal Feed	56750	50848	71749
gms	wt%	wt%	wt%
C	65.0	63.0	65.0
H	4.9	4.9	4.8
O	11.6	13.4	11.1
N	1.2	1.2	1.2
S	3.6	3.6	3.7
Ash	13.7	13.9	14.2
Moisture	3.7	5.5	2.7
Fixed Carbon	44.5	43.0	45.1
Volatile Matter	38.1	37.6	38.0
Water	95350	88757	110549
gms	wt%	wt%	wt%
H	11.1	11.1	11.1
O	88.9	88.9	88.9
Oxygen[1/]	20884	18614	21338
gms	wt%	wt%	wt%
O	100.0	100.0	100.0
Nitrogen[2/]	84802	82567	89117
gms	wt%	wt%	wt%
N	100.0	100.0	100.0

[1/] Not analyzed

[2/] Not analyzed

Table 3. Streams from the gasifier (tests 162, 163, 164)

	162	163	164
Condensate gms	81723	75894	90721
	wt%	wt%	wt%
C	1.6	1.6	1.6
H	10.9	10.9	10.9
O	87.0	87.0	87.0
S	0.5	0.5	0.5
Filter Dust gms	684	269	871
	wt%	wt%	wt%
C	75.0	72.8	74.9
H	1.7	1.7	1.9
O	2.1	2.2	2.0
N	0.8	0.8	0.9
S	1.3	1.4	1.4
Extractor Hopper gms	12939	11804	22019
	wt%	wt%	wt%
C	50.9	61.3	48.7
H	0.7	0.7	0.6
N	0.3	0.4	0.3
S	0.6	0.7	0.5
Tar gms	1844	1368	2920
	wt%	wt%	wt%
C	83.0	82.8	83.1
H	6.4	6.3	6.4
O	6.4	6.0	6.4
N	1.2	1.2	1.3
S	2.7	2.6	2.7
Gas gms	154682	143195	206444
	wt%	wt%	wt%
C	15.2	14.2	15.1
H	2.6	2.5	2.6
O	26.5	24.8	23.4
N	54.8	57.7	43.2
S	0.9	0.9	1.0
Gasifier[1] gms	3355	2740	590
	wt%	wt%	wt%
C	69.3	62.6	60.8
H	0.8	1.0	1.2
O	0.7	1.5	0.9
N	0.4	0.6	0.9
S	0.8	1.1	1.4

[1] Char left in gasifier at the end of run.

DISCUSSION OF RESULTS

Table 1 shows the overall results of 3 tests. They were roughly duplicates of each other; for example, the percent steam decomposition and percent carbon gasified for each experiment are in good agreement with each other.

Tables 2 and 3 show the feed plus product streams of the gasifier. Table 4 shows the overall weight balances of the five main components for each test. As can be seen, they are good—ranging from 96 percent to 100 percent. Table 5 shows the analysis of 65 trace elements made by spark source mass spectrometry. The results in this table are reported as ppm wt. (µg/g) while the water is reported as µg/ml. It is recognized that higher accuracy can be achieved and will be done on selected elements in the next series of tests rather than getting so many analyses. However, it is believed for this first attempt that the coverage of elements analyzed should be as wide as possible. Some of these values on the feed coal do not agree with Ruch (ref. 4).

Table 4. Overall mass balances of the major components (tests 162, 163, 164)

	Σ In kg	Σ Out kg	% Recovery
162			
C	36.9	35.8	97.0
H	13.4	13.3	99.5
O	112.2	112.2	100.0
N	85.5	84.9	99.3
S	2.0	2.0	100.0
163			
C	32.0	31.8	99.4
H	12.3	12.1	97.6
O	104.3	101.7	97.4
N	83.2	82.6	99.4
S	1.8	1.8	100.0
164			
C	46.6	46.7	100.2
H	15.7	15.4	98.2
O	127.6	127.4	99.9
N	89.9	89.2	99.2
S	2.7	2.6	96.3

Table 6 shows the percent recovery of 16 selected elements which are considered the most important of the 65 analyzed. While the elements Hg, U, As, Zn, Mn, Cr, V, P, F, B, and Be indicate some reasonable degree of recovery, Pb, Cd, Se, Ni, are too inaccurate. Other elements, while not listed in table 6 are as inaccurate as Sr, Fe,and Al. It is recognized that SSMS values are usually considered good to within a factor of 3.

These wide ranges, both plus and minus, would indicate more precise analytical methods are needed to get better yield data.

Tables 7, 8,and 9 show where these trace elements are in the various streams for 3 experiments. The first part of each table was made by totalling the yields from the gasifier and then, calculating of the total, where the percentage of the elements are in the water, tar, fines, and char. The second part shows how much of the feed quantities are found in each of the off streams. It is seen (table 9) in both cases that the greatest percentage of the 16 elements (remembering the accuracy discussed with table 6) is in the chars and dusts except Hg, B, Se, and F, some of which are found in the water. Almost all of the chlorine is in the water. The tars contain some As, Pb, Cd, and Hg. While the determinations of elemental analysis of the feed water and off-gas were incomplete and not used, it is believed these are too small to affect the balances. This belief is strengthened by the analysis shown in TPR-6 (ref. 3) in the gas.

Table 10 shows the results of a comparison of trace element concentrations in the condensate from the gasifier compared to the same type analysis on a Monongahela River sample. As can be seen, except for elements such as B, Hg,and Se, in many cases the percentages of the trace elements is actually higher in the river water.

CONCLUSIONS

These three gasifier tests made in the small PDU gasifier at Bruceton, Pa., indicate that the trace elements primarily remain in the chars and dusts emanating from the gasifier. Some elements, such as boron, chlorine, fluorine, and selenium are found in the water and some such as arsenic, lead, and cadmium are in the tars. Of course, the high sulfur percentage in the tars was already known from the major component analysis. Further tests are needed to concentrate on better analyses of fewer elements to obtain greater accuracy and better balances. Unfortunately, the mercury analyses were incomplete, but most of the mercury appears in the tar and water, with little remaining in the char or dust.

Table 5A. Trace element analysis of all streams (test 162)

162	Feed Coal ppm (ug/g)	Filter Fines ppm (ug/g)	Char ppm (ug/g)	Tar ppm (ug/g)	H_2O ppm (ug/g)
Ag	0.01	<0.01	<0.05	-	-
Al	>0.5%	540	1800	29	0.007
As	0.87	3.7	6.5	0.71	0.001
B	86	64	380	12	43
Ba	170	130	98	3.6	0.10
Be	1.5	7.2	4.6	0.03	-
Bi	<0.10	<1.7	<0.44	0.20	-
Br	0.23	0.65	1.6	0.02	0.001
Ca	>1%	>0.5%	>1%	450	2.4
Cd	0.097	0.88	1.6	-	-
Ce	47	25	54	0.29	-
Cl	93	11	33	1.5	300
Co	14	17	95	0.09	0.002
Cr	170	47	240	7.1	0.043
Cs	0.26	1.2	0.65	-	-
Cu	39	70	40	0.74	0.003
Dy	1.4	3.9	1.6	-	-
Er	2.1	0.41	0.80	-	-
Eu	0.55	0.39	0.65	-	-
F	490	610	150	0.97	39
Fe	>1%	>0.5%	>1%	240	0.081
Ga	8.3	3.6	4.5	0.08	-
Gd	1.9	1.2	0.48	-	-
Ge	1.1	1.3	5.4	0.08	-
Hf	0.83	3.5	11	-	-
Hg	0.10	0.20	*	1.2	0.027
Ho	0.43	0.16	0.45	-	-
I	0.4	1.9	0.27	0.02	-
K	>1%	190	5400	14	0.31
La	22	6.7	17	0.03	-
Li	0.8	34	67	0.51	0.001
Lu	0.085	<0.18	0.40	-	-
Mg	2800	4600	3500	240	0.57
Mn	160	48	240	2.2	0.20
Mo	15	21	14	0.31	-
Na	1900	>1%	4700	360	6.6
Nb	4.7	7	13	0.08	-
Nd	23	19	11	0.06	-
Ni	43	12	25	1.2	0.018
P	130	460	460	14	0.04
Pb	0.55	2.2	21	0.22	0.003
Pr	7.3	7.5	4.2	0.02	-
Rb	180	36	27	0.10	-
S	>1%	7700	2100	120	1.6
Sb	0.18	0.04	1.9	-	-
Sc	5.3	6.4	17	0.02	-
Se	2.2	15	4.7	0.23	0.14
Si	>1%	>1%	>1%	500	2.8
Sm	2.7	0.30	0.86	0.01	-
Sn	0.6	0.75	1.9	0.03	-
Sr	3.3	44	70	4.5	0.12
Ta	0.73	0.64	1.2	-	-
Tb	0.2	0.20	0.89	-	-
Te	<0.29	<0.19	0.15	-	-
Th	3	5.8	4.3	0.06	-
Ti	880	1800	3300	8.4	0.003
Tl	<0.12	<0.19	<0.25	0.11	-
Tm	0.24	0.10	0.20	-	-
U	1.4	5.6	5.4	0.01	-
V	100	44	190	0.21	-
W	0.08	2.2	4.8	0.09	-
Y	21	37	48	0.10	-
Yb	0.35	2.7	2.2	-	-
Zn	25	11	100	0.48	0.13
Zr	10	22	28	0.26	-

*Insufficient results.

Table 5B. Trace element analysis of all streams (test 163)

163	Feed Coal ppm (μg/g)	Filter Fines ppm (μg/g)	Char ppm (μg/g)	Tar ppm (μg/g)	H_2O ppm (μg/g)
Ag	<0.009	<0.054	<0.054	-	-
Al	2400	1000	790	30	0.006
As	1.3	6.5	3.3	1.6	<0.001
B	86	32	300	52	17
Ba	190	80	98	6.0	0.095
Be	1.3	4.6	2.1	0.07	-
Bi	<0.10	3.1	1.2	0.17	-
Br	0.13	3.2	1.6	0.08	-
Ca	>1%	>0.5%	>1%	2000	3.6
Cd	0.097	1.6	0.77	0.15	-
Ce	22	22	89	1.5	-
Cl	220	33	14	1.2	170
Co	6	4.1	9.5	0.35	-
Cr	100	120	120	10	0.004
Cs	0.13	0.33	0.65	0.04	-
Cu	27	18	40	6.4	0.002
Dy	0.7	1.21	3.4	0.10	-
Er	1.6	0.40	0.54	-	-
Eu	<0.22	0.65	1.3	0.02	-
F	420	740	320	12	37
Fe	>0.5%	>1%	>1%	530	0.18
Ga	5.8	2.1	2.1	0.17	-
Gd	0.081	0.48	0.95	0.01	-
Ge	2.1	2.5	2.5	0.08	-
Hf	0.73	2.2	1.1	0.04	-
Hg	0.14	0.07	*	0.47	0.029
Ho	0.19	0.30	0.30	-	-
I	0.23	2.7	0.23	0.08	-
K	>0.5%	2300	2300	130	0.46
La	11	7.7	7.7	0.16	-
Li	0.8	38	38	0.48	0.001
Lu	<0.081	0.35	0.40	-	-
Mg	1600	3500	3500	820	1.0
Mn	220	140	500	4.7	0.01
Mo	11	14	28	0.32	-
Na	1900	>0.5%	>1%	780	6.8
Nb	4.7	13	6.5	0.18	-
Nd	23	4.6	11	0.31	-
Ni	10	11	25	1.6	0.002
P	63	1100	2100	31	0.04
Pb	1.1	8.9	21	0.48	0.002
Pr	7.3	1.8	4.2	0.12	-
Rb	67	23	27	1.1	-
S	>1%	4300	2100	1000	0.74
Sb	0.10	0.95	0.95	-	-
Sc	7	8.3	8.3	0.10	-
Se	1.2	4.7	4.7	0.24	0.002
Si	>1%	>1%	>1%	4000	4.7
Sm	1.1	0.86	1.7	0.04	-
Sn	1.0	1.4	1.9	0.07	-
Sr	2.3	33	70	9.8	0.055
Ta	0.31	1.2	1.2	0.02	-
Tb	0.086	0.11	0.22	-	-
Te	<0.29	<0.11	<0.11	-	-
Th	6.4	4.3	9.2	0.21	-
Ti	800	590	1700	67	-
Tl	<0.12	<0.25	<0.25	0.24	-
Tm	0.24	0.12	0.13	-	-
U	3	2.7	14	0.06	-
V	43	41	95	2.6	0.001
W	<0.024	4.8	9.6	0.21	-
Y	10	9.5	20	0.37	-
Yb	0.4	0.96	0.96	0.03	-
Zn	49	48	100	3.3	0.007
Zr	4.8	9.3	28	0.57	-

*Insufficient results.

Table 5C. Trace element analysis of all streams (test 164)

164	Feed Coal ppm (µg/g)	Filter Fines ppm (µg/g)	Char ppm (µg/g)	Tar ppm (µg/g)	H_2O ppm (µg/g)
Ag	0.013	<0.09	0.21	-	-
Al	2000	330	3200	20	0.009
As	1.5	6.1	2.9	1.1	0.001
B	86	40	160	12	82
Ba	83	80	140	1.5	0.058
Be	0.64	2.6	5.7	0.05	-
Bi	<0.10	1.5	<0.99	<0.30	-
Br	0.13	0.75	1.9	0.01	0.001
Ca	>1%	3500	>1%	240	2.0
Cd	0.087	0.73	1.4	-	-
Ce	16.5	16	15	0.20	-
Cl	93	6.7	14	0.42	190
Co	3.5	11	10	0.24	-
Cr	100	29	220	3.0	0.006
Cs	0.13	0.73	0.69	-	-
Cu	39	23	22	0.86	0.003
Dy	1.1	1.8	3.8	-	-
Er	1.6	0.8	0.57	-	-
Eu	<0.22	0.21	0.34	-	-
F	280	690	240	1.4	32
Fe	>1%	>1%	>1%	200	0.11
Ga	1.9	2.3	4.6	0.02	-
Gd	1.4	0.37	0.35	-	-
Ge	0.91	1.9	7.6	0.02	0.001
Hf	0.66	1.4	0.45	-	-
Hg	0.08	0.06	0.04	0.21	0.030
Ho	0.13	0.16	0.15	-	-
I	0.4	1.4	<0.20	-	0.001
K	>1%	190	5400	14	0.31
La	>0.5%	2300	2300	130	0.46
Li	0.4	21	40	0.33	-
Lu	<0.081	0.14	0.12	-	-
Mg	800	4400	2700	360	0.32
Mn	220	40	160	1.6	0.014
Mo	6.3	13	25	0.11	0.001
Na	1900	>1%	>1%	530	5.4
Nb	4.7	8.7	4.1	0.03	-
Nd	9.9	12	11	0.09	-
Ni	10	18	25	0.95	0.001
P	130	>1%	630	9.1	0.022
Pb	0.55	2.8	5.7	0.16	-
Pr	7.3	3.5	4.4	0.04	-
Rb	25	4.9	54	0.06	-
S	>0.5%	4800	2300	42	0.57
Sb	0.1	0.06	0.11	-	-
Sc	7	8	11	0.01	-
Se	0.58	9.3	3.8	0.08	0.18
Si	>1%	>1%	>1%	742	6.6
Sm	1.1	0.43	0.61	0.10	-
Sn	0.45	0.93	0.88	0.02	-
Sr	15	59	55	2.4	0.034
Ta	0.73	0.8	0.16	-	-
Tb	0.086	0.12	0.12	-	-
Te	<0.029	<0.12	0.16	-	-
Th	4.5	5.1	4.9	0.04	-
Ti	800	1100	1100	8.1	0.036
Tl	<0.12	<0.12	<0.11	0.16	-
Tm	0.24	0.15	0.14	-	-
U	3	5	4.7	0.02	-
V	35	50	47	0.31	0.002
W	<0.024	1.9	2.9	0.02	-
Y	10	23	22	0.07	-
Yb	0.28	1.7	1.6	-	-
Zn	49	28	66	1.4	0.096
Zr	10	31	13	0.08	-

Table 6. Trace element balances of selected components

	Σ In mg	Σ Out mg	% Recovery		Σ In mg	Σ Out mg	% Recovery
162				163 (con.)			
As	49.4	109.9	222.5	Mn	11186.6	7317.0	65.4
B	4880.5	9771.8	200.2	Ni	508.5	369.0	72.6
Be	85.1	79.9	93.9	P	3203.4	30884.4	964.1
Cd	5.5	26.7	485.5	Pb	55.9	308.6	552.1
Cl	5277.7	25065.0	474.9	Se	61.0	70.6	115.7
Cr	9647.5	3959.4	41.0	U	152.5	204.5	134.1
F	27807.5	6050.4	21.8	V	2186.5	1396.4	63.9
Hg	5.7	4.6	80.7	Zn	2491.6	1472.5	59.1
Mn	9080.0	3963.9	43.7				
Ni	2440.3	419.3	17.2	164			
P	7377.5	7839.2	106.3	As	107.6	74.2	69.0
Pb	31.2	344.4	1103.7	B	6170.4	11126.5	180.3
Se	124.9	788.5	631.3	Be	45.9	131.3	286.1
U	79.5	100.0	125.8	Cd	6.2	32.3	521.0
V	5675.0	3126.4	55.1	Cl	6672.7	17560.7	263.2
Zn	1418.8	1648.5	116.2	Cr	7174.9	5008.6	69.8
				F	20089.2	8934.3	44.5
163				Hg	5.7	4.3	75.4
As	66.1	52.0	78.7	Mn	15784.8	3658.3	23.2
B	4372.9	5951.9	136.1	Ni	717.5	583.9	81.4
Be	66.1	31.9	48.3	P	9327.4	14280.0	153.1
Cd	4.9	11.8	240.8	Pb	39.5	131.8	333.7
Cl	11186.6	15302.9	136.8	Se	41.6	111.2	267.3
Cr	5084.8	1791.6	35.2	U	215.2	110.7	51.4
F	21356.2	8153.6	38.2	V	2511.2	1107.2	44.1
Hg	7.1	3.2	45.1	Zn	3515.7	1529.5	43.5

Table 7. Percentage of selected components in major effluent streams (test 162)

162	Out mg	H_2O %	Tar %	Char %	Fines %
As	109.9	0.1	1.2	96.4	2.3
B	9771.8	36.0	0.2	63.4	0.4
Be	79.9	-	0.1	93.8	6.1
Cd	26.7	-	-	97.7	2.3
Cl	25065.0	97.8	0.1	2.1	0.0
Cr	3959.4	0.1	0.3	98.8	0.8
F	6050.4	52.7	0.0	40.4	6.9
Hg*					
Mn	3963.9	0.4	0.1	98.7	0.8
Ni	419.3	0.4	0.5	97.1	2.0
P	7839.2	0.0	0.3	95.7	1.3
Pb	344.4	0.1	0.1	99.4	0.4
Se	788.5	1.5	0.1	97.1	1.3
U	100.0	-	0.0	96.2	3.8
V	3126.4	0.0	0.0	99.0	1.0
Zn	1648.5	0.6	0.0	98.9	0.5

	In mg	H_2O %	Tar %	Char %	Fines %
As	49.4	0.2	2.7	214.4	5.2
B	4880.5	72.0	0.5	126.9	0.9
Be	85.1	0.0	0.1	88.1	5.8
Cd	5.5	0.0	0.0	474.0	10.9
Cl	5277.7	464.5	0.05	10.2	0.14
Cr	9647.5	0.1	0.1	40.5	0.3
F	27807.5	11.5	0.0	8.8	1.5
Hg	5.7	38.9	39.1	-	2.5
Mn	9080.0	0.2	0.1	43.1	0.4
Ni	2440.3	0.1	0.1	16.7	0.3
P	7377.5	0.1	0.4	101.6	4.3
Pb	31.2	0.7	1.3	1096.7	4.8
Se	124.9	9.6	0.3	613.1	8.2
U	79.5	0.0	0.1	120.9	4.8
V	5675.0	0.0	0.1	54.6	0.5
Zn	1418.8	0.8	0.1	114.8	0.5

*Insufficient results

Table 8. Percentage of selected components in major effluent streams (test 163)

163	Out mg	H_2O %	Tar %	Char %	Fines %
As	52.0	0.3	4.2	92.2	3.3
B	5951.9	25.4	1.2	73.3	0.1
Be	31.9	-	0.3	95.9	3.8
Cd	11.8	-	1.7	94.8	3.5
Cl	15302.9	98.6	0.0	1.3	0.1
Cr	1791.6	0.0	0.8	97.4	1.8
F	8153.6	40.3	0.2	57.1	2.4
Hg*					
Mn	7317.0	0.0	0.1	99.4	0.5
Ni	369.0	0.1	0.6	98.5	0.8
P	30884.4	0.0	0.1	98.9	1.0
Pb	308.6	0.1	0.2	98.9	0.8
Se	70.6	1.0	0.4	96.8	1.8
U	204.5	-	0.0	99.6	0.4
V	1396.4	0.0	0.3	98.9	0.8
Zn	1472.5	0.0	0.3	98.8	0.9

	In mg	H_2O %	Tar %	Char %	Fines %
As	66.1	0.2	3.3	72.6	2.7
B	4372.9	34.5	1.6	99.8	0.2
Be	66.1	0.0	0.2	46.3	1.8
Cd	4.9	0.0	4.1	228.6	8.8
Cl	11186.6	134.9	0.01	1.8	0.08
Cr	5084.8	0.0	0.3	34.3	0.6
F	21356.2	15.4	0.1	21.8	0.9
Hg	7.1	36.1	9.0	-	0.3
Mn	11186.6	0.0	0.1	65.0	0.3
Ni	508.5	0.1	0.4	71.5	0.6
P	3203.4	0.1	1.3	953.4	9.2
Pb	55.9	0.3	1.2	546.3	4.3
Se	61.0	1.1	0.5	112.1	2.1
U	152.5	0.0	0.1	133.6	0.5
V	2186.5	0.0	0.2	63.2	0.5
Zn	2491.6	0.1	0.2	58.4	0.5

*Insufficient results

Table 9. Percentage of selected components in major effluent streams (test 164)

164	Out mg	H_2O %	Tar %	Char %	Fines %
As	74.2	0.3	4.3	88.3	7.1
B	11126.5	66.9	0.3	32.5	0.3
Be	131.3	-	0.1	98.2	1.7
Cd	32.3	-	-	98.0	2.0
Cl	17560.7	98.2	0.0	1.8	0.0
Cr	5008.6	0.0	0.2	99.3	0.5
F	8934.3	32.5	0.0	60.8	6.7
Hg	4.3	63.5	14.3	21.0	1.2
Mn	3658.3	0.0	0.1	98.9	1.0
Ni	583.9	0.0	0.5	96.8	2.7
P	14280.0	0.0	0.2	99.7	0.1
Pb	131.8	-	0.4	97.8	1.8
Se	111.2	15.3	0.2	77.2	7.3
U	110.7	-	0.1	96.0	3.9
V	1107.2	0.0	0.1	96.0	3.9
Zn	1529.5	0.6	0.3	97.5	1.6

	In mg	H_2O %	Tar %	Char %	Fines %
As	107.6	0.1	3.0	60.2	4.9
B	6170.4	120.6	0.6	58.6	0.6
Be	45.9	0.0	0.2	280.8	5.0
Cd	6.2	0.0	0.0	509.7	11.5
Cl	6672.7	258.3	0.02	4.7	0.09
Cr	7174.9	0.0	0.1	69.3	0.4
F	20089.7	14.5	0.0	27.0	3.0
Hg	5.7	47.4	10.6	15.7	0.9
Mn	15784.8	0.0	0.0	22.9	0.2
Ni	717.5	0.1	0.4	78.8	2.2
P	9327.4	0.1	0.3	152.7	0.1
Pb	39.5	0.0	1.2	326.3	6.2
Se	41.6	40.8	0.6	206.5	19.5
U	215.2	0.0	0.1	49.4	2.0
V	2511.2	0.0	0.1	42.3	1.7
Zn	3515.7	0.3	0.1	42.4	0.7

Table 10. Trace element analysis of Monongahela riverwater and an earlier gasification condensate

	Mon River: 12th St. Bridge, Pgh ppm (vol)	Synthane CHPFI-120 ppm (vol)		Mon River: 12th St. Bridge, Pgh ppm (vol)	Synthane CHPFI-120 ppm (vol)
Ag	0.025	0.009	Na	16	0.22
Al	0.13	2.7	Nb	-	0.040
As	0.010	0.071	Nd	0.017	-
B	0.24	85	Ni	-	0.11
Ba	0.50	0.51	P	0.17	0.40
Br	0.041	0.017	Pb	0.021	0.032
Ca	25	1.5	Rb	0.31	0.77
Cd	-	-	S	21	NR*
Ce	0.003	0.005	Sb	0.009	0.032
Cl	3.8	0.41	Sc	0.012	0.025
Co	0.005	0.031	Se	-	1.1
Cr	0.004	0.029	Si	16	43
Cs	0.015	0.015	Sm	0.011	-
Cu	0.012	0.013	Sn	-	0.13
Fe	0.88	0.90	Sr	0.56	0.28
Ga	0.007	0.014	Ti	2.2	1.1
Ge	0.020	0.038	U	0.025	0.025
Hg	<0.0001	0.015	V	0.008	0.008
I	0.005	0.033	W	-	-
K	1.8	<0.1	Y	0.01	0.009
La	0.016	0.036	Zn	0.40	0.17
Li	-	0.01	Zr	0.043	0.028
Mg	6.5	0.39			
Mn	0.19	0.008			
Mo	4.9	1.8			

*Not reported due to matrix difficulties

-Less than 0.001 mg/ml (ppm)

ACKNOWLEDGMENTS

We acknowledge with thanks the help of our analytical groups at Bruceton; especially the General Analysis Group headed by H. Schultz, with special thanks to W. McKinstry, F. E. Walker, J. F. Smith, M. J. Mima, and M. F. Ferrer. Other in-house analyses were done by the Spectro-Physics Group headed by R. A. Friedel. The trace analyses were handled by A. G. Sharkey through arrangements with Accu-Lab Co., Wheaton, Colorado.

REFERENCES

1. R. R. Bertrand and C. E. Jahnig, "A Look at Environmental Aspects of Coal Conversion," American Chemical Society, Division of Fuels Chemistry, Philadelphia, Pa., April 7-11, 1975.
2. A. Attari, M. Mensinger, and J. C. Pau, "Fate of Trace Constituents of Coal During Gasification" (Part II), American Chemical Society Division of Fuel Chemistry, Philadelphia, Pa., April 7-11, 1975.
3. A. J. Forney, W. P. Haynes, S. J. Gasior, G. E. Johnson, and J. P. Strakey, Jr., "Analysis of Tars, Chars, Gases and Water Found in Effluents from the Synthane Process," BuMines TPR 76, January 1974, 9 pp.
4. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: A Final Report," Environmental Geological Notes, No. 72, Illinois Geological Survey, Urbana, Ill., August 1974.

CO_2 ACCEPTOR PROCESS

Carl Fink, George Curran, and John Sudbury*

Abstract

Recent operation of the CO_2 Acceptor Process pilot plant has demonstrated that the gasifier product gas contains no detectable amounts of tars, oils, phenols, or cyanides. Three key process advantages also have been confirmed: (1) suitable synthesis gas is made without the use of an oxygen plant, (2) no water-gas shift plant is required, and (3) gasifier product gas cleanup is simplified because the gas contains less H_2S and CO_2 than in any other process. Significant progress has been made toward improving reliability of plant operation.

INTRODUCTION

The CO_2 Acceptor Process, a fluidized bed system to convert lignite or subbituminous coal to pipeline gas, is undergoing testing on a pilot plant scale at Rapid City, South Dakota. The demonstration program is being carried out by Conoco Coal Development Company under contract with the Energy Research and Development Administration and the American Gas Association.

Description of the Process

A schematic diagram of the CO_2 Acceptor Process is shown in figure 1. There are two fluidized bed reactors, a gasifier, and a regenerator which operate at a pressure of 150 psig. Lignite or subbituminous coal is fed to the bottom of the gasifier where, after rapid hydrodevolatilization, gasification of fixed carbon with steam occurs. The gasifier temperature is in the range of 1480° F to 1550° F. Heat for the gasification reactions is supplied by a circulating stream of lime-bearing material called acceptor. The acceptor, which can be either limestone or dolomite, supplies heat needed for gasification principally by the exothermic CO_2 acceptor reaction:

$$CaO + CO_2 = CaCO_3$$
$$\Delta H = -76{,}200 \text{ Btu/lb mole } (77° F)$$

The CO_2 acceptor reaction is reversed in the regenerator at about 1850° F where heat is supplied by burning the residual char from the gasifier with air. Ash is removed from the regenerator by elutriation and collected via an external cyclone and lockhopper system. Seals between the gasifier and regenerator are maintained by purged standlegs of solids.

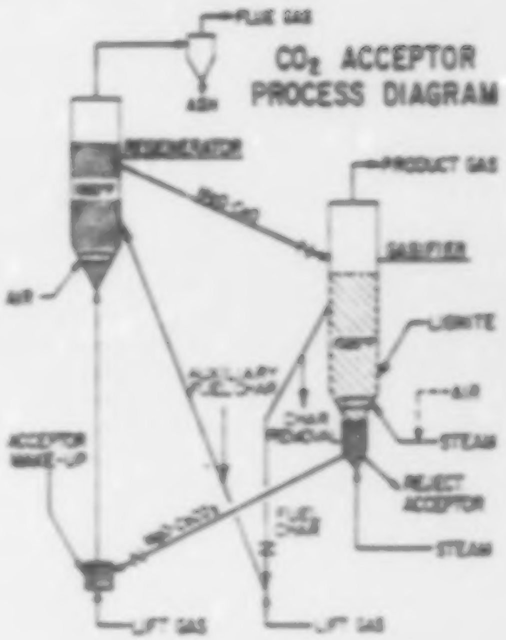


Figure 1. CO_2 acceptor process diagram.

Since the acceptor loses reactivity to the CO_2 acceptor reaction as it circulates between the reactors, some of the circulating inventory purposely is withdrawn from the gasifier and replaced with fresh stone makeup. The makeup is added to the acceptor which is returning to the regenerator.

SUMMARY

Since October 1974, 7 runs have been made in the Rapid City pilot plant bringing the total to 28. The last 3 runs in this series were of sufficient length and smoothness to provide process heat and material balance data. The final run, Run 28, featured 12 days of integrated operation at process temperatures, nearly 10 days in which the acceptor supplied the entire gasifier heat duty, and 3 days of steady-state plant operation. Major accomplishments of these runs include:

1. Demonstration that the accumulation of intermediate fines in the gasifier char bed can be successfully controlled (Runs 26, 27, and 28).

---

*The authors are with the Conoco Coal Development Company, Library, Pennsylvania.

2. Demonstration of gasifier operation with no recycle gas dilution of the inlet steam (Runs 27 and 28).
3. Accomplishment of a smooth, orderly plant shutdown (Run 27).
4. The successful use of limestone quarried in Rapid City as a CO_2 acceptor (Run 28).

The problems and progress in plant operation since February of 1974 are summarized in table 1. This table lists the problems encountered and the accomplishments of all the runs since Run 17. Problems resulting in run termination are indicated as are the solutions of plant problems. During the year, a major process problem—the accumulation of intermediate fines in the gasifier char bed—was solved by adding a lockhopper system to continuously remove a slip stream of solids from the char bed. A major effort towards establishing plant reliability was made following Run 25. The goal of this effort was to make mechanical and procedural revisions where necessary to eliminate plant upsets. The success of Runs 26, 27, and 28 shows that this goal is near at hand.

The results of Runs 26, 27, and 28 have reaffirmed the advantages of the CO_2 Acceptor Process:

1. The ability to produce a synthesis gas suitable for conversion to pipeline gas without the use of oxygen.
2. The absence of hydrocarbons other than CH_4 in the gasifier product gas.
3. Substantially total carbon utilization as shown by the fact that the carbon contained in the ash removed from the regenerator is less than 1 percent of the carbon in the feed.
4. A ratio of H_2 to CO in the product which exceeds 3:1, such that all of the CO and part of the CO_2 can be methanated with no water-gas shift required.
5. Low concentrations of CO_2 and H_2S in the product gas which reduce the gas cleanup requirements.

PLANT OPERATION

Solution of the Intermediate Fines Accumulation Problem

Last year it was reported that a major process problem had surfaced during Run 21. Particles too large to be elutriated from the regenerator with the char ash and too small to be removed with the reject acceptor, accumulated in the gasifier char bed affecting the ability to maintain a stable char-acceptor interface. After 10 days' operation during Run 21, these particles accounted for 34 percent by weight of the gasifier char bed. Removal of a slip stream of gasifier char bed material into lockhoppers has solved this problem entirely. The level of intermediate fines in the gasifier char bed was controlled throughout Run 28 which was 12 days in duration. The char withdrawal rate was set such that the intermediate fines level was essentially constant at 10 percent during the final 6 days of the run. In a commercial plant, the purged char bed material could be ground to a size which permits the intermediate fines to be elutriated from the regenerator bed with the char ash. This ground material would be returned to the regenerator thus minimizing the thermal penalty.

Mineral impurities existing in the coal seam are the source of these intermediate fines. In the Velva lignite and Husky char, these impurities are principally grains of α quartz. Figure 2 shows the percent grains by weight plotted against the weight percent SiO_2 in the Velva lignite and Husky char. The percent grains were determined by ashing the coal and screening the ash residue. The portion of the residue that cannot be crushed and forced through a 200 Tyler mesh screen is the grains fraction. The figure illustrates that the fraction of the coal which forms intermediate fines (grains) is directly proportional to the silica content of the feedstock. The quartz grains react with char ash and attrited acceptor forming intermediate fines.

In the plant, the char withdrawal stream is removed from the standleg through which the regenerator fuel char flows. During Run 28, 200 lbs/hr of material were withdrawn to maintain the intermediate fines level at 10 percent. The char content of the withdrawn material was about 52 percent by weight. The intermediate fines problem had been solved during Run 23. Early in that run, the char withdrawal rate was too low and the intermediate fines concentration in the gasifier char bed built up to a potentially dangerous level. The level of intermediate fines concentration was then reduced to an operable level by minimizing the lignite feed rate and maximizing the char withdrawal rate. During this operation, the weight of intermediate fines in the system was decreased by 1100 lbs in 26 hours. Thus, the ability to recover from an accumulation of intermediate fines has been demonstrated.

Although the silica content and, therefore, intermediate fines potential may vary in different feedstocks, the char removal approach offers a means of coping with the problem. Five runs have been made since Run 23, and no problems related to intermediate fines accumulation have occurred.

Improvement of Plant Reliability

Even though the intermediate fines problem had been solved, the plant did not operate reliably during Runs 24 and 25. Problems existed primarily in two areas of the plant, the gasifier quench system and the fuel char standleg which includes the char removal lockhoppers. Following Run 25, a major effort was made to make

Table 1. Problems and progress in CO_2 acceptor process

Run No.	17	18	19	20	21	22	23	24	25	26	27	28
Date	Feb 22 Apr 2 1976	Apr 19 Apr 29 1976	June 5 July 17 1976	Aug 2 Aug 19 1976	Aug 30 Sept 15 1976	Sept 20 Dec 22 1976	Jan 7 Feb 5 1975	Feb 21 Mar 14 1975	Mar 31 Apr 10 1975	May 17 June 17 1975	June 27 Aug 12 1975	Aug 26 Sept 27 1975
Mechanical Problems:												
Carburization Attack of Gasifier Heater Coils	▨	*										
Weld Failure - Gasifier Internal Cyclone				▩	*							
Stress Corrosion Cracking - Cold Expansion Joints			▩		▨	▩	*					
Miscellaneous - Feed Preparation System		▨					▨			▨		
Lift Line Erosion (Misaligned Slip Joints)							▩					
Plugs in Gasifier Quench System		▨				▨	▨	▩		*		
Char Withdrawal Lockhopper Pressure Upsets						▨	▨	▨	▩	*		
Weld Failure Butterfly Valve											▩	*
Utility Power Failure										▩	▨	
Reject Acceptor Lockhopper Upsets												▨
Problems with Solids Sample Station	▩											▩
Process Problems												
Accumulation of Intermediate Fines					▩	▨	▨	*				
Process Accomplishments												
Integrated Plant Operation	■	■	■	■	■	■	■	■	■	■	■	■
Six Days or More	■	■	■		■		■	■		■	■	■
Supplied All Process Heat by Circulating Acceptor	■		■	■	■	■	■			■	■	■
100 Percent Replacement of Dead-Burned Dolomite					■		■			■	■	■
Successful Gasification of Raw Lignite			■	■	■	■	■	■	■	■	■	■
Obtained Heat and Material Balance Data	■		■	■	■					■	■	■
100 Percent Steam to Gasifier											■	■
Rapid City Limestone as Acceptor												■
Orderly Shutdown											■	
Lignites with Higher Sodium Content as Feedstock												
Subbituminous Coal as Feedstock												
Operation of Turbine Test Stand												
Methanation												

*Problem substantially solved

▩ Caused termination of run

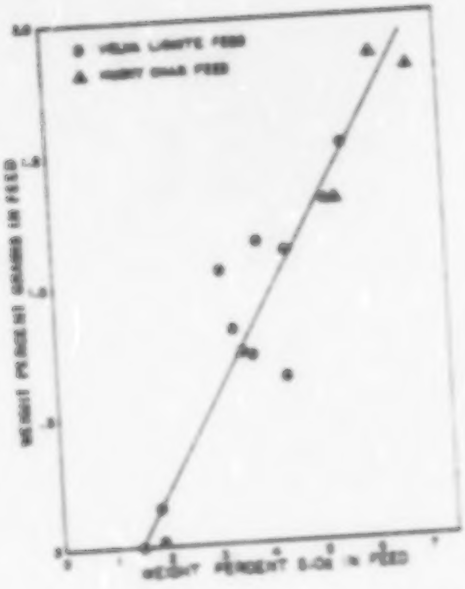


Figure 2. Weight percent grain vs. weight percent SiO_2 in gasifier feedstock.

these systems reliable. A comprehensive review of past experience led to mechanical modifications and operating procedure revisions. This approach has led to three consecutive data producing runs.

During Runs 22 through 25, deposits built up in the venturi scrubber at the inlet to the gasifier quench tower. In the extreme, Run 24, the deposit plugged the inlet to the quench tower stopping the flow of gas from the gasifier thus terminating the run. Analysis of the deposits showed them to be principally calcium carbonate. The source of the calcium carbonate was the char ash and the city water used as scrubber water. Solutions to the problem were carried out in three areas: (1) revision of the water dispersion pattern in the venturi scrubber; (2) initiation of water treatment as advised by Betz Laboratories, Inc.; and (3) installation of rod-out devices to remove deposits before they result in upsets. During subsequent runs, there have been no major upsets associated with the gasifier quench system.

The fuel char standleg had become very sensitive to upsets after the char removal system was installed. Upsets would occur as the withdrawal flow was switched from one of the parallel lockhoppers to the other. Occasionally, these upsets caused the standleg to plug interrupting fuel char flow. An upset of this nature ended Run 25. Following Run 25, the fuel char standleg system was extensively modified. The modifications included: (1) revision of the configuration and control of the char withdrawal lockhoppers [series rather than parallel lockhoppers]; (2) revision of the fuel char standleg instrumentation and control; and (3) addition of an auxiliary char system to supply char fuel to the regenerator, in an emergency, from the lockhoppers rather than from the gasifier.

These modifications have improved the reliability of the fuel char standleg and char withdrawal systems. This reliability was an important factor in the success of the runs that followed.

Plant reliability continues to be a major goal of the program. The 12 days of plant operation during Run 28 are evidence that achievement of this goal is close at hand.

Use of Auxiliary Fuel

Auxiliary fuel, originally conceived as an emergency alternate to fuel char from the gasifier, has become a useful process tool. There are two streams containing char which leave the gasifier and are not returned to the regenerator. These two streams, the overhead char loss through the cyclone and the reject char to the char removal lockhoppers, represent a major thermal penalty in the operation of the pilot plant. In a commercial plant, these streams would be ultimately returned to the regenerator. Auxiliary fuel can be used to simulate the return of these char streams to the regenerator. Table 2 illustrates this concept using Run 26 as an example. The table shows these two streams and their heats of combustion. The sum of their heats of combustion is 1.8 million Btu/hr, 6.5 percent of the heat of combustion of the lignite feed. This is not a process inefficiency but rather a pilot plant loss. the addition of 100 lb/hr of auxiliary fuel with a heat of combustion of 1.1 million Btu/hr accounts for 61 percent of this nonprocess penalty.

Achievements During Successful Runs

Runs 26, 27, and 28 were all of sufficient duration and smoothness to provide process data. The log of days of operation at key conditions is shown in table 3. In these runs, as in Run 21, the minimum requirements for steady-state operation were achieved. These minimum requirements are: (1) the total replacement of the start-up dead-burned dolomite inventory, and (2) the use of circulating acceptor to supply all of the gasifier heat duty. Unlike Run 21, process conditions were not changing due to the accumulation of intermediate fines in the gasifier char bed. However, very slow unidirectional changes prevented the achievement of long periods of

Table 2. Use of auxiliary fuel during run 26

Char Loss From Gasifier	Lbs/hr	Heat of Combustion MM Btu/hr
Char Withdrawal	76	0.828
Char Loss Overhead	112	1.006
Total		1.834
Auxiliary Fuel Char	100	1.120

Net Heat Loss As Char = 1.834 - 1.120 = .714 MM Btu/Hr

Table 3. Log of operations runs 26, 27, and 28

Run No.	26	27	28
Days			
Integrated Plant Operation at Process Temperature	6.0	10.1	12.0
Lignite Feed	5.3	9.8	11.3
Dolomite Makeup	5.6	9.0	-
Limestone Makeup	-	-	11.2
All Heat Supplied by Acceptor	2.7	2.7	9.6
All Dead-Burned Dolomite Replaced	.5	4.0	5.0
Gasifier With 100 Percent Steam	0	1.0	3.8
Steady-State Plant Operation	0	0	3.0

truly steady-state operation during Runs 26 and 27. In Run 26 the acceptor activity increased slowly and, as a result, the acceptor circulation had to be reduced. In Run 27 minor upsets resulted in the use of a small amount of air in the gasifier between the two air-free periods. Truly steady-state operation was achieved during Run 28. The plant operated for 12 days at process temperatures, including nearly 10 days without air in the gasifier and 3 days at steady-state.

Other major achievements of Runs 27 and 28 include the demonstration of gasifier operation in the absence of recycle gas (Runs 27 and 28), the performance of a smooth, orderly shutdown (Run 27), and the use of limestone as acceptor (Run 28). Also, a comprehensive set of solids and liquid samples were collected during smooth periods of Runs 27 and 28 for detailed analysis including trace elements.

In all runs prior to Run 27, some recycle gas was mixed with the gasifier inlet steam. Early laboratory work had shown that the acceptor will agglomerate at steam partial pressures of 13 atmospheres or greater; therefore, some caution has been exercised in demonstrating the no recycle operation. The gasifier has now been operated without recycle gas in the gasifier inlet gas for 1 day during Run 27 and for nearly 4 days during Run 28. There have been no problems attributable to operation without recycle gas.

As shown in table 1, Run 27 was terminated when the weld failed on the butterfly valve which controls the rate of regenerator fuel char flow from the gasifier to the regenerator. When this problem was recognized, the plant was shut down in a smooth, orderly fashion. Subsequent inspection of the gasifier and regenerator reactors showed that no deposits had formed after 10 days of operation at temperature.

Since gasification of lignite was first begun during

Run 19, Tymochtee dolomite from Ohio has been the acceptor used. A principal purpose of Run 28 was to test the Minnekahta limestone which is quarried at Rapid City as the CO_2 acceptor. The geographic location of the Minnekahta stone is such that it can be considered as a potentially economical acceptor in a commerical plant. Also, since it is a limestone, it can be reconstituted using a process which has been demonstrated by Conoco on a bench scale. The experience of Run 28 in which limestone makeup was fed for 11 days proved this limestone to be a satisfactory CO_2 acceptor. There were no problems which could be attributed to the use of limestone. The measured activity of the equilibrium limestone acceptor inventory was quite similar to that observed with the Tymochtee dolomite when expressed on a weight of CO_2 accepted per unit weight of stone basis.

Sets of samples representing all of the major solids and liquid streams were obtained during a smooth period at the end of Run 27 and also during the steady-state period of Run 28. Each of these samples will be thoroughly analyzed by the South Dakota School of Mines. The concentrations of trace elements will be determined for all samples. Although the analyses are not yet complete, early results are encouraging. The gasifier quench water was found to contain no detectable phenols or cyanides.

DETAILED RUN DATA (RUN 26)

Although a true steady-state condition was not achieved during Run 26, the changes occurring were very slow and unidirectional. The slow trend towards higher acceptor activity and lower acceptor circulation has no discernible effect on the lignite feed rate, the regenerator duty, or the yield and composition of the gasifier product gas. Neither the detailed data from Run 27 nor the steady-state operation data from Run 28 are presented since analyses of the key solids streams have not yet been completed.

Heat and Material Balances

A detailed heat and material balance representing a smooth period at the end of Run 26 is shown in table 4. Since there is no direct measurement of either the fuel char rate or the acceptor circulation rate, detailed plant results are calculated by the simultaneous solution of the heat balance and elemental balances. The heat balance for Run 26 is summarized in table 5.

During Run 26, 2,450 lb/hr of Velva lignite were fed to the gasifier and 56,400 SCFH of product gas were produced. As shown in table 4, the heat of combustion of the product gas was 76.9 percent of that of the lignite feed. This is despite the inefficiencies inherent in pilot plant operation which include:

1. Large plant heat losses.
2. Char losses from the gasifier in excess of those compensated for by the use of auxiliary fuel.
3. Large sensible heat duty from the use of a large amount of regenerator recycle gas.

The data from Run 26 confirm the excellent carbon utilization of the CO_2 Acceptor Process. The ash exiting from the regenerator contains only 0.65 percent of the carbon in the lignite feed. The gasifier cyclone loss and the char withdrawal loss account for 7.5 percent of the carbon in the lignite feed. However, the addition of the carbon in the auxiliary fuel (to simulate partial char recovery) reduced the net carbon loss to 3 percent of the lignite feed. High carbon utilization has been demonstrated in all of the data producing runs made in the pilot plant.

In Run 26, as in all of the runs made with no air input to the gasifier, the ratio of H_2 to CO in the gasifier product gas was in excess of the 3:1 requirement for methanation. In Run 26, the ratio was 3.8:1. As a result, all of the CO and about 34 percent of the CO_2 could be converted to CH_4. Gas cleanup would also be simplified by the absence of hydrocarbons other than methane. Only removal of NH_3, H_2S, and part of the CO_2 are required prior to methanation.

The data obtained from steady periods of plant operation have been consistent with projections made from the bench-scale data and those projected for use in commercial designs.

Pressure Balance Relationships

Since Run 16, over 2300 hours of acceptor circulation at process temperatures have been logged. The ability to circulate acceptor and to feed fuel char from the gasifier to the regenerator is dependent upon maintaining a system pressure balance. Figure 3 shows the static pressures at 15 key points in the reactor-standleg-lift line system. These data correspond to the conditions shown in table 4 for Run 26.

EXPERIMENTAL PROGRAM

The immediate experimental goals in the Rapid City pilot plant are as follows:

1. Operation of the packed tube methanation unit.
2. Testing of possible turbine blade materials for use in power recovery from the regenerator flue gas stream.
3. Testing the use of two additional lignites. Feedstocks having higher sodium contents than Velva lignite.
4. Testing the use of subbituminous coal as gasifier feedstock.

Table 4. Heat and material balance, run 26, 2000 hours, June 15, 1975, system pressure – 150 PSIG

Basis: 1 hour
Datum: H_2O (l) at 60°F

GASIFIER

	Lbs.	SCF	°F	M Btu Sensible Heat	M Btu Heat of Combustion
Input					
Lignite(1)	2,050		400	253.453	27025.979
Acceptor(8)	8,795		1800	3830.364	
Boot Gas			1430		
Recycle(9)	846	10,077		421.603	
Steam	1,573	33,062		2726.700	
Ring Gas			1505		
Steam	1,046	22,080		1830.654	
Purge			60		
Recycle(9)	106	1,210			
Inert(11)	43	580			
N_2	70	1,070			
Subtotal	16,550			9062.863	27025.979
Heats of Reaction					
$CaO+CO_2=CaCO_3$ 30.07 Mols @ 76,300 Btu/Mol				2294.273	
Total				11357.136	
Output					
Char			1495		
To Regenerator(2)	623			325.354	6881.600
Reject(2)	75			39.163	828.404
Char Loss From Cyclone(3)	112			55.438	1000.129
Acceptor(7)			1495		
To Regenerator	9,709			3522.531	
Reject	317			114.626	
Gas			1495		
Product(9)	3,066	56,369		1777.457	21040.800
Recycle(9)	577	17,205		545.356	
Steam	1,220	25,664		2357.886	
H_2S	6	69		2.520	43.978
NH_3	10	308		17.305	173.017
Subtotal	16,550			8557.190	30157.208
Heats of Reaction					
Heat of Combustion (Output Input as Acceptor)				2511.269	
$CaO+S=CaS+O$ 0.23 Mols @ 196,540 Btu/Mol				45.375	
Heat Loss				243.295	
Total				11357.135	

REGENERATOR

	Lbs.	SCF	°F	M Btu Sensible Heat	M Btu Heat of Combustion
Input					
Char(2)	623		1495	325.154	6881.600
Auxiliary Fuel(5)	100		60		1119.000
Acceptor					
From Gasifier(7)	9,709		1495	3522.531	
Makeup(6)	400		60		
Air(12)	5,755	75,340	830	1006.102	
H_2O	21	440		29.587	
Acceptor Lift(10)	4,306	50,857	1175	1236.221	
H_2O	14	297		22.605	
Char Lift Gas			725		
Inert Gas(11)	553	7,006		80.062	
Recycle(10)	200	2,873		59.603	
H_2O	1	17		1.007	
Purge			60		
Recycle(10)	165	1,916			
Inert(11)	18	238			
N_2	9	119			
Subtotal	22,217			6361.935	8001.379
Heats of Reaction					
Heat of Combustion (Output Input as Acceptor)				7162.227	
$CaS+O=CaO+S$ 0.03 Mols @ 196,540 Btu/Mol				4.923	
Total				13529.085	
Output					
Char(4)	103		1800	65.980	150.530
Acceptor(8)			1800		
To Gasifier	8,795			3830.364	
Overhead	40			21.191	
Gas			1800		
Flue Gas(10)	7,330	96,559		2972.681	700.537
Recycle(10)	4,796	51,667		2209.096	
Steam	97	2,045		101.242	
COS	1	7		0.260	3.640
H_2S	1	6		0.473	4.038
SO_2	2	14		0.502	
Subtotal	22,217			10351.230	859.352
Heats of Reaction					
$MgCO_3=MgO+CO_2$				150.000	
$CaCO_3=CaO+CO_2$				2423.100	
Heat Loss				506.712	
Total				13509.099	

LIGNITE CHAR

	(1)	(2)	(3)	(4)	(5)
Moisture, Wt %	0	0	0	0	3.86
Moisture Free Basis, Wt %					
H	4.50	0.83	0.70	0.00	7.20
C	66.36	73.29	59.30	7.50	76.30
N	1.00	0.36	0.22	0.00	0.90
O	20.87	0.00	0.00	0.00	7.10
S	0.54	0.00	0.00	0.00	1.50
Ash (as oxides)	6.84	18.70	33.05	90.70	14.00
CaS-CaO	0.00	0.07	0.00	1.03	0.00
CO_2	0.00	6.75	6.30	0.00	0.00

ACCEPTOR

Wt %	(6)	(7)	(8)
MgO	22.04	36.02	41.23
CaO	27.08	43.42	49.71
Inert	4.93	7.03	9.06
CO_2	45.65	17.61	0.00
CaS-CaO	0.00	0.03	0.00
Activity		0.370	

GAS

Mol %	(9)	(10)	(11)	(12)
CH_4	13.75	0.00	0.00	0.00
H_2	50.00	0.06	0.00	0.00
CO	15.47	2.24	0.00	0.00
CO_2	9.00	29.35	12.40	0.00
N_2	7.91	68.00	88.00	79.00
O_2	0.00	0.00	0.00	21.00

Table 5. Summarized heat balance
run 26

	MM Btu/Hr	%
In		
Lignite Feed, Heat of Combustion	27.826	100.00
Out		
Heats of Combustion		
Gasifier Streams		
Product Gas	21.404	76.92
Net Char [(1)]	.714	2.57
NH_3 & H_2S	.217	0.78
Regenerator Streams		
Flue Gas + H_2S + COS	.708	2.54
Overhead Ash	.151	0.54
Net Heats of Reaction		
$MgCO_3$ = $MgO+CO_2$	.150	0.54
$CaCO_3$ = $CaO+CO_2$	.130	0.47
CaO+S = CaS+O	.041	0.15
Sensible Heats		
Outlet Streams - Inlet Streams	3.481	12.51
Heat Losses		
Gasifier	.243	0.87
Regenerator	.587	2.11
	27.826	100.00

(1) Net char = Heat of combustion of the char losses not compensated for by the use of auxiliary fuel (see table 2).

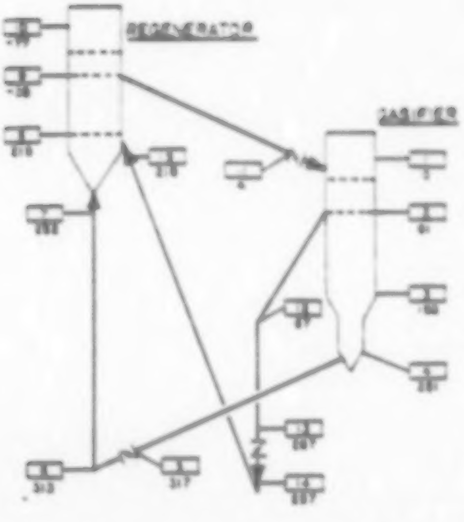


Figure 3. Pressure balance diagram.

operated. The fixed blade turbine test stand is installed and ready for operation. Testing will begin when a suitable steady-state condition is achieved. Some caution will be exercised as operation of this unit could easily upset the gasifier-regenerator pressure balance.

Bench-scale runs have shown that lignite with a very high sodium content (14 percent of the sulfur free ash) may form deposits in the gasifier fluidized bed and, therefore, not be useful as feedstock. A run will be made using Glenharold lignite containing about 7 percent sodium on the sulfur free ash. This lignite, which is now stockpiled in Rapid City, has a higher content of sodium in the ash than most North Dakota lignites. Glenharold lignite having an even higher sodium content is available and will be purchased for use in future runs.

Subbituminous coal from Montana has been purchased and is stockpiled in Rapid City. A run or series of runs will be made to determine the performance of this coal as a feedstock for the CO_2 Acceptor Process.

EFFLUENT CONSIDERATIONS IN COAL GASIFICATION

Frank C. Schora and Donald K. Fleming*

Abstract

Several processes are being considered for the conversion of coal into high-Btu gas. The HIGAS Process, now being developed at the pilot-plant level under ERDA/AGA funding, is the furthest advanced of these processes and has operated for extended periods on U.S. coals.

The HIGAS Process is based on the utilization of high-pressure operation and close control of gas-solids contacting in three countercurrent stages. These operating conditions promote the direct production of methane within the gasifier, maximizing the process efficiency by utilizing the heat of methane formation directly within the gasifier, thereby minimizing heat requirements from other sources. Under the conditions of gasification, high yields of methane are achieved – nearly 70 percent of the feed product methane is produced in the gasifier. The operating conditions of the HIGAS reactor apparently also inhibit the production of tar and heavy liquids that are made in moving-bed gasifiers. Similarly, the conditions of operation tend to produce simple sulfur compounds, apparently by hydrocracking of the heavier sulfur complexes found in coal. Therefore, the HIGAS reactor generally tends to minimize the formation of materials that may be classed as pollutants. Depending upon the gas processing train prior to final methanation, these potential pollutants can be reasonably well-controlled, and emissions from the facility can be held to reasonable limits.

The exact quantities of such materials, which would be produced from various coals under consideration for gasification, remain to be established in the program.

INTRODUCTION

This discussion has been prepared as an overview on the environmental aspects of coal gasification. For several years, the Institute of Gas Technology (IGT) has been evaluating coal gasification from an environmental viewpoint, based both on the overall process concept and our own specific processes. This discussion presents some of our findings in this area and also indicates where environmental data are lacking.

The primary IGT objective in gasification development has been directed at the proof of the overall hydrogasification concept, with specific emphasis upon gasifier design and operation. The IGT effort in the environmental area has necessarily been modest because it is primarily funded in-house. Now that we have successfully demonstrated, in a large pilot plant, the viability of more efficient, second-generation coal gasification, we anticipate that additional effort will be expended in defining the possible discharges to the environment.

Magnitude of Energy Problem

Figure 1 presents a projection of possible energy supply-demand relationships for the United States through the next 25 years. The discussion of the data behind this graph is a long dissertation in itself; we will only touch upon the highlights here:

- The energy demand is based on a 3.7 percent annual growth rate in the *per capita* energy requirements, a rate that appears necessary to sustain our economy.
- The energy supply is based upon maximum conventional utilization of our indigenous energy resources including –
  - The maximum projected expansion of nuclear power generation (without limitations of capital availability or construction moratoria).
  - Maximum increase in the drilling rate for crude oil and natural gas (without the reduction in finding rate that has recently been experienced).
  - Maximum increase in direct coal utilization (assuming transportation and environmental limitations are overcome).
- The noncrosshatched area of figure 1 indicates the energy shortfall that must be eliminated, either by imports or development of nonconventional energy resources.

Obviously, we must develop all of our energy resources, including oil shale, coal conversion and other sources, if we are to maintain our economic independence.

To make this energy shortfall more meaningful, consider the energy output from one 250 million SCF/day coal gasification facility. The coal feedstock requirement is 6-8 times the amount required for a coal-based ammonia plant of 1000 ton/day capacity. The energy output is nearly identical to 3000 megawatts-thermal power generation, but is equal to only about 40,000 bbl/day of oil – 25 such coal plants are required to equal the million bbl/day goal that has been set in Project Independence to reduce our oil imports.

Coal Utilization–Environmental Aspects

We Americans must develop all of our energy resources and, by far, our largest resource is coal.

---

*The authors are with the Institute of Gas Technology, Chicago, Illinois.

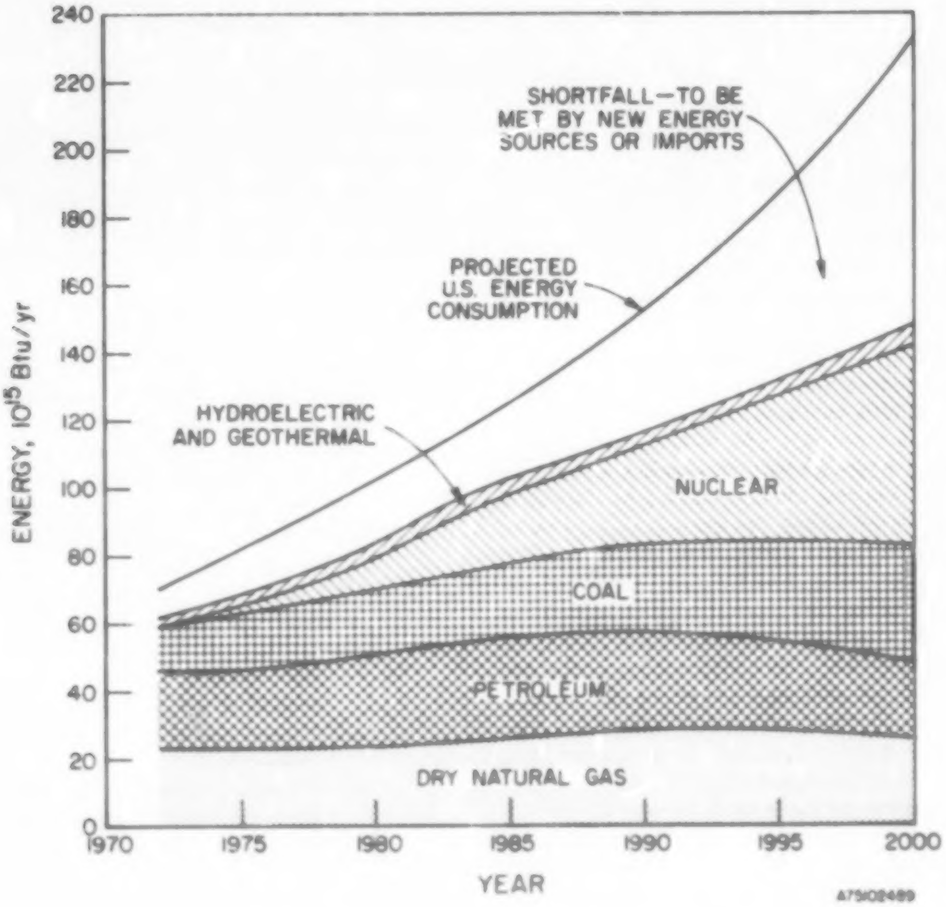


Figure 1. Possible energy supply-demand relationships in the United States projected over the next 25 years.

Unfortunately, coal is not a "nice" fossil fuel. Significant environmental problems must be overcome by an energy use that is based upon coal. Some of the problems that must be faced, in one form or another, in any coal utilization scheme include:

- Fate of sulfur present in coal.
- Fate of nitrogen in coal.
- Fate of other nonhydrocarbon material in coal, including chlorine, trace elements, and, of course, the large ash disposal problem.
- Fate of possible products of incomplete or side reactions in coal utilization, including carbon monoxide, tars, oils, soot, or other materials.
- Environmental problems related to large-scale coal mining.
- The aesthetic effect of the necessarily large coal piles required to maintain production.

COMPARISON: ENVIRONMENTAL ASPECTS OF COAL GASIFICATION AND DIRECT COMBUSTION

The gasification of coal appears to be an environmentally and economically preferred method of coal utilization, compared to direct combustion, as illustrated by the estimated data in table 1. (Most of the data presented in table 1 will be discussed later.) First, we should list a number of the qualifications that underlie these data.

The comparison is based upon a net resultant product of residential thermal energy. We recognize that

Table 1. SNG manufacture vs. electricity generation

	GAS PLANT 250 X 10^6 SCF/day (> 3000 MW thermal)	POWER PLANT 3000 MW electric
COAL FEEDSTOCK, tons/day (12,500 Btu/lb, 4% sulfur)	15,000	30,000
Disposal		
Ash, tons/day	1,500	3,000
Lime sludge from stack clean-up (tons/day $CaSO_3 \cdot 2H_2O$)	475	4,750
Other sludges	≥ 200	
Anticipated emissions		
Power plant		
SO_x, tons/day	45	450
NO_x, tons/day	26	260
Particulate, tons/day	3.75	37.5
Process		
Claus tail gas		
Sulfur species, tons/day as S	0.75	
CO_2 Vent gas		
Sulfur species, tons/day as S	5	
Hydrocarbon, tons/day	0–200	
Wastewater		
Cooling tower blowdown, gpm	0–750	
Estimated Capital Cost*	$1 billion	$2 billion
*Cost of Product, $/$10^6$ Btu		
At Plant gate	2.59	10.01
As residential heat	4.99 (hot air heat at 75% eff.)	15.30 (resistance heat at 100% eff.)

*Early 1975 basis

electricity is thermodynamically equivalent to work; however, as long as a significant sector of energy planning recommends electrification of our energy base, degrading much of that electricity into residential heat, the comparison is valid. The basis for production of electricity is 33 percent net thermal efficiency (including efficiency losses necessary for stack-gas scrubbing). The stack-gas scrubbing system is assumed to be a first-generation lime treatment technique, and is assumed to meet Federal EPA New Source Performance Standards for SO_x, NO_x, and particulate discharges.

The basis for projection of emissions from high-Btu gas production is less firm and the data presented in table 1 are, therefore, only approximations. Not only do we have significant data gaps in estimating potential emissions, but the problem is further compounded by the number of variables that must be considered:

- *Variety of Coal Feedstocks.* Coal is not a simple material and its composition, including its potential for formation of possible pollutants, will vary widely, depending on the coal source.
- *Variety of Gasifier Configurations.* A wide variety of gasifiers is either available, under development, or proposed. Each of these systems has different operating conditions of temperature, pressure, number of stages, and gas-solid contacting mode. Therefore, each of these gasifiers has a different potential for generation of potential pollutants from the constituents in

the raw coal. This is the primary area where gasification developers, such as IGT, can influence the overall emissions from the facility. We believe that our concepts, although developed for maximum gasification efficiency, will also result in systems that have reduced overall emissions of potential pollutants.

- *Variety of Treatment Processes.* In this area, the engineering contractor integrates the gasifier into an overall system; many options are available for purification of the raw gas in the overall facility. The engineering contractor defines the design philosophy that will determine most of the overall emissions. Such design philosophies might include:
  - *Incineration of any hydrocarbon-containing stream.* We have seen this design philosophy in several proposed systems, although, as we discuss later, the energy cost is excessive.
  - *Waste water management.* We have seen designs that recycle water to extinction and others that propose a liquid discharge stream from the facility. This point will also be discussed later.
  - *Minimum control systems with absolute minimum facility capital cost.* We have not yet seen this design philosophy, but this is the possible approach that concerns the EPA in its studies of coal gasification emissions.

With these qualifications in mind, we can consider the data of table 1. First, the generation of electricity uses twice the coal feedstock as the production of an equivalent amount of thermal energy in the form of gas. Therefore, the generation of electricity for residential heating will deplete our reserves about twice as rapidly. With twice the feedstock requirement, electrical power generation must also dispose of twice the quantity of ash.

By far the greatest source of sulfur emissions from a typical gasification facility is the on-site boiler house, even when it releases SO_2, NO_x and particulates in conformance with Federal New Source Performance Standards. The quantities of these pollutants that may reach the atmosphere are a factor of 10 lower in the coal gasification facility than in the electric power plant.

Other advantages of the coal gasification facility include a significantly reduced energy cost, both at the plant (or bus bar) and as actually consumed in the residence when the inefficiencies of transmission and utilization are considered.

On the other side of the ledger, the gas plant has environmental deficits in some areas compared to electric generation. For example, the process area of the gasification plant will emit sulfur that does not have a direct counterpart in the electric facility. We anticipate that most of this sulfur will be carbonyl sulfide, an odorless sulfur species that is considered comparable to or even environmentally preferred to sulfur dioxide according to a recent study for the EPA. Even with the sulfur emitted from the process area, the overall sulfur emissions from the gasification plant are still a factor of 7 less than the electric power plant of comparable output.

The gas facility also has a potential for hydrocarbon emissions. In some combinations of gasifiers and purification systems, the hydrocarbon emissions may be quite low. In some process flow sheets, the expected hydrocarbon emissions are primarily methane, a nonreactive hydrocarbon. And, as mentioned before, some engineering contractors, to play safe, will incinerate any steam containing hydrocarbons, even at high cost.

Most gasification processes will also have solid discharges of sludges from raw-water and wastewater treatment and the potential of a wastewater discharge from the facility (although perhaps not to the local watershed), depending upon the design philosophy of the engineering contractor.

On the balance, the production of high-Btu gas appears to be an environmentally preferred alternative for the manufacture of clean energy from coal.

TYPICAL COAL GASIFICATION EMISSIONS

Figure 2 presents a block flow diagram of a coal gasification facility that might be constructed in the future. Note that the gasifier developer is responsible for just 1 or 2 of the 20 blocks on this diagram—the gasifier and perhaps a pretreater. The engineering contractor will select and integrate the remainder of the subsystems into an overall facility. Fully half of the blocks on this diagram are shaded, indicating purification processes that are primarily responsible for the overall environmental control of the facility. It is obvious that a large fraction of the overall cost of the facility may be ascribed to environmental control.

On this block flow diagram, there are three primary points for gaseous discharge from the plant — the boiler house stack, the Claus plant off-gas, and the CO_2-rich gas that must be vented from the process. Solids disposal consists of ash, lime-scrubbing sludge, and water-treatment sludges. Additionally, there is potential for an aqueous liquid discharge stream from the process.

We will now consider how the gasifier configuration—the province of developers such as IGT—can affect potential emissions in the discharges.

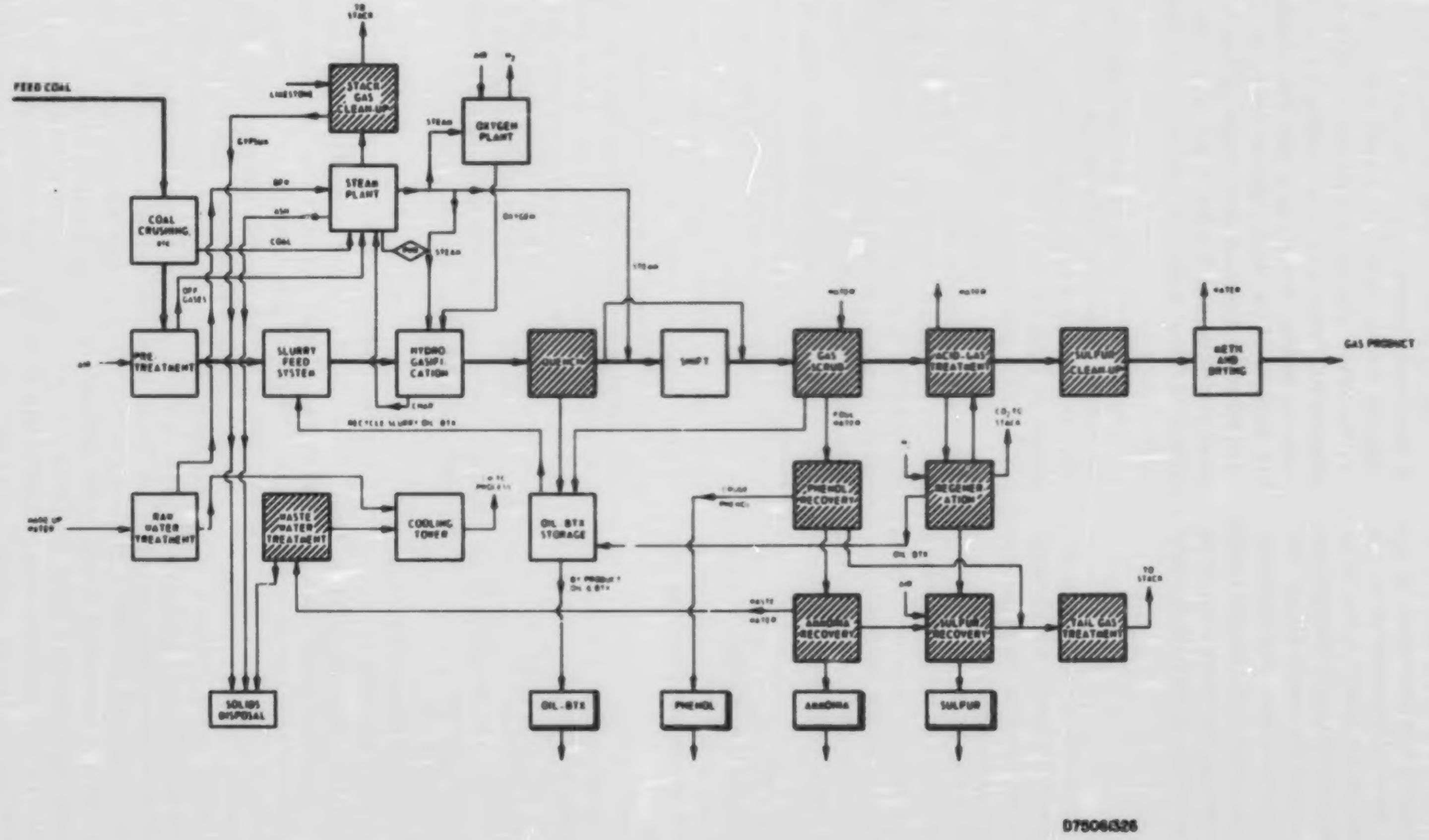

FEED COAL
COAL CRUSHING, etc
PRE-TREATMENT
air
OFF GASES
TO STACK
STACK GAS CLEAN-UP
LIMESTONE
GYPSUM
BFW
ASH
COAL
STEAM PLANT
STEAM
OXYGEN PLANT
air
N_2
OXYGEN
STEAM
SLURRY FEED SYSTEM
HYDRO GASIFICATION
CHAR
RECYCLE SLURRY OIL BTX
QUENCH
SHIFT
GAS SCRUB
water
FOUL WATER
ACID-GAS TREATMENT
water
CO_2 TO STACK
SULFUR CLEAN-UP
METH AND DRYING
water
GAS PRODUCT
MAKE UP WATER
RAW WATER TREATMENT
WASTE WATER TREATMENT
COOLING TOWER
OIL BTX STORAGE
BY PRODUCT OIL & BTX
PHENOL RECOVERY
CRUDE PHENOL
REGENERATION
OIL BTX
WASTE WATER
AMMONIA RECOVERY
air
SULFUR RECOVERY
TAIL GAS TREATMENT
TO STACK
SOLIDS DISPOSAL
OIL-BTX
PHENOL
AMMONIA
SULFUR
D75061326

Figure 2. Block-flow diagram of a coal gasification facility.

Surprisingly, the maximum effect is found in the boiler-house stack. Although the concentrations of pollutants in this gas are regulated, the quantity of fuel consumed in the boiler house is a direct function of the efficiency of the process, and the gasifier configuration has a pronounced effect upon the overall process efficiency. The gasifier configuration also has an influence, but a lesser effect, upon the constituents that are present as impurities in the CO_2-vent gas, the composition of the discharged ash, and contaminants in the possible wastewater from the facility.

Process Efficiency

The primary influence on the overall process efficiency is the configuration of the gasifier and its effect in favoring certain chemical reactions. In the overall process flowsheet, the total chemical reaction is:

$$2C + 2H_2O \rightarrow CO_2 + CH_4 \qquad (1)$$

Theoretically this overall reaction should be highly efficient. However, when we mix coal with water, nothing happens. As we increase the temperature to about 1800° F, we find that the coal and water react, endothermically, to form carbon monoxide and hydrogen (not methane):

$$C + H_2O \rightarrow CO + H_2 \qquad (2)$$

The heat required to sustain this reaction must be supplied from an outside source and the mechanism of this heat supply is one of the primary variables in system concept and gasifier design.

After the coal has been steam-gasified to carbon monoxide and hydrogen, the ratio of these two species is adjusted by converting some of the carbon monoxide into additional hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

Then, the final product, methane, can be manufactured from the carbon monoxide and hydrogen:

$$CO + 3H_2 \rightarrow H_2O + CH_4 \qquad (4)$$

The reaction to form methane is exothermic and could, thermodynamically, offset the heat required for the steam-carbon reaction. However, the methanation reaction takes place at lower temperatures (700°-900° F) and is not useful for supplying the heat required for the steam-carbon reaction at 1800° F.

Generally, when we follow the chemical reaction system outlined above, according to the older technology that can presently be employed for coal gasification, the heat required to sustain the steam-carbon gasification must be added to the gasifier itself at 1800° F or higher. The most common way to supply this heat is to add oxygen directly into the gasifier and burn some of the carbon from the original coal. With the direct utilization of steam-oxygen-carbon gasification, the primary chemical reactions for gasification can be represented in the flowsheet of figure 3.

The oxygen for the process is separated from air by power—usually steam power. The steam and oxygen loads for the process are the primary energy consumers for the overall process, as indicated in figure 4. This diagram was based upon data available for the energy loads for an older technology process and indicates that the majority of the steam raised in the boiler house is used either for process steam or oxygen production. The total energy demand for this boiler house (for a 250 million SCF/day facility) is equivalent to a 500 megawatt power plant.

One goal of the developers of the newer processes has been to reduce this energy demand. The technique used for improvement of overall process efficiency is called hydrogasification. In this system, the coal is reacted directly with hydrogen according to the reaction:

$$C + 2H_2 \rightarrow CH_4 \qquad (5)$$

This direct methanation reaction is exothermic and the heat of this reaction can be used to offset the heat required by the steam carbon reaction. The hydrogen required for the direct methanation reaction is produced by steam-oxygen-carbon gasification. In the flowsheet of figure 5, the more reactive constituents of the coal are hydrogasified and the less reactive carbon in the coal is used to manufacture the required hydrogen. The resulting steam and oxygen requirements for the overall facility are significantly reduced, perhaps to about 300 megawatt equivalent heat load for the boiler house. Therefore, the boiler house emissions expected for the older technology processes are perhaps 67 percent higher than will be anticipated for the newer systems. Referring back to table 1, the boiler house was the major source of emissions from the overall process of coal gasification and the emissions quoted in table 1 were based upon newer technology, not the higher emissions expected from older processes.

Claus Plant Off-Gas

The gasifier developer can have only a modest effect upon the potential pollutants that are present in the final off-gas from the sulfur plant in the facility. The engineering contractor will determine the number of stages for the Claus plant and the process that is used for tail gas purification. Until specific standards are set for coal refineries, the engineer will probably attempt to meet those standards that have been set for petroleum refineries — 300 ppm total sulfur in the undiluted gas. We emphasize that this standard is based upon petroleum refineries where the sulfur concentration in the initial feed to the sulfur plant will be relatively high. The standard may be unrealistically low for coal refineries where high concentrations of carbon dioxide will exist in the sulfur plant feed. Indeed, for most viable systems of

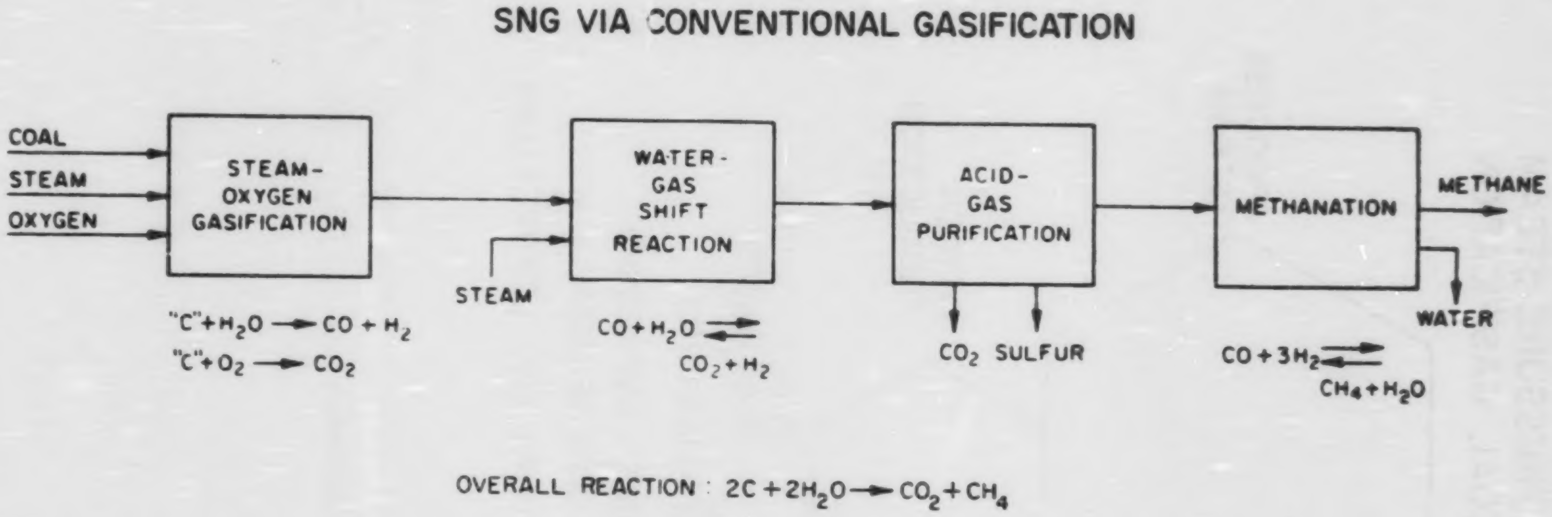

SNG VIA CONVENTIONAL GASIFICATION
COAL
STEAM
OXYGEN
STEAM-OXYGEN GASIFICATION
"C"+H2O → CO + H2
"C"+O2 → CO2
STEAM
WATER-GAS SHIFT REACTION
CO+H2O ⇌ CO2+H2
ACID-GAS PURIFICATION
CO2
SULFUR
METHANATION
CO+3H2 ⇌ CH4+H2O
METHANE
WATER
OVERALL REACTION : 2C+2H2O → CO2+CH4

Figure 3. Pipeline gas production using conventional gasification.

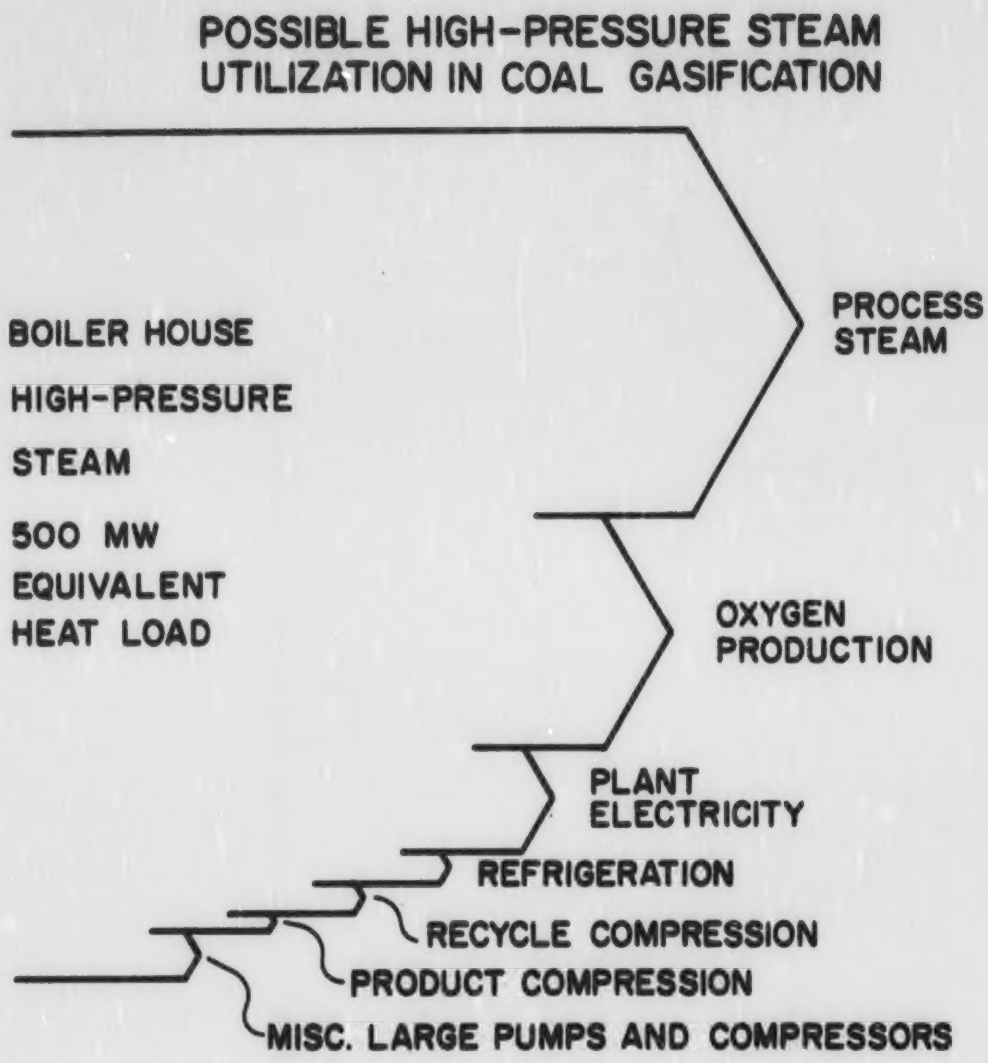

POSSIBLE HIGH-PRESSURE STEAM UTILIZATION IN COAL GASIFICATION
BOILER HOUSE
HIGH-PRESSURE
STEAM
500 MW
EQUIVALENT
HEAT LOAD
PROCESS STEAM
OXYGEN PRODUCTION
PLANT ELECTRICITY
REFRIGERATION
RECYCLE COMPRESSION
PRODUCT COMPRESSION
MISC. LARGE PUMPS AND COMPRESSORS

Figure 4. Possible high-pressure steam utilization in coal gasification.

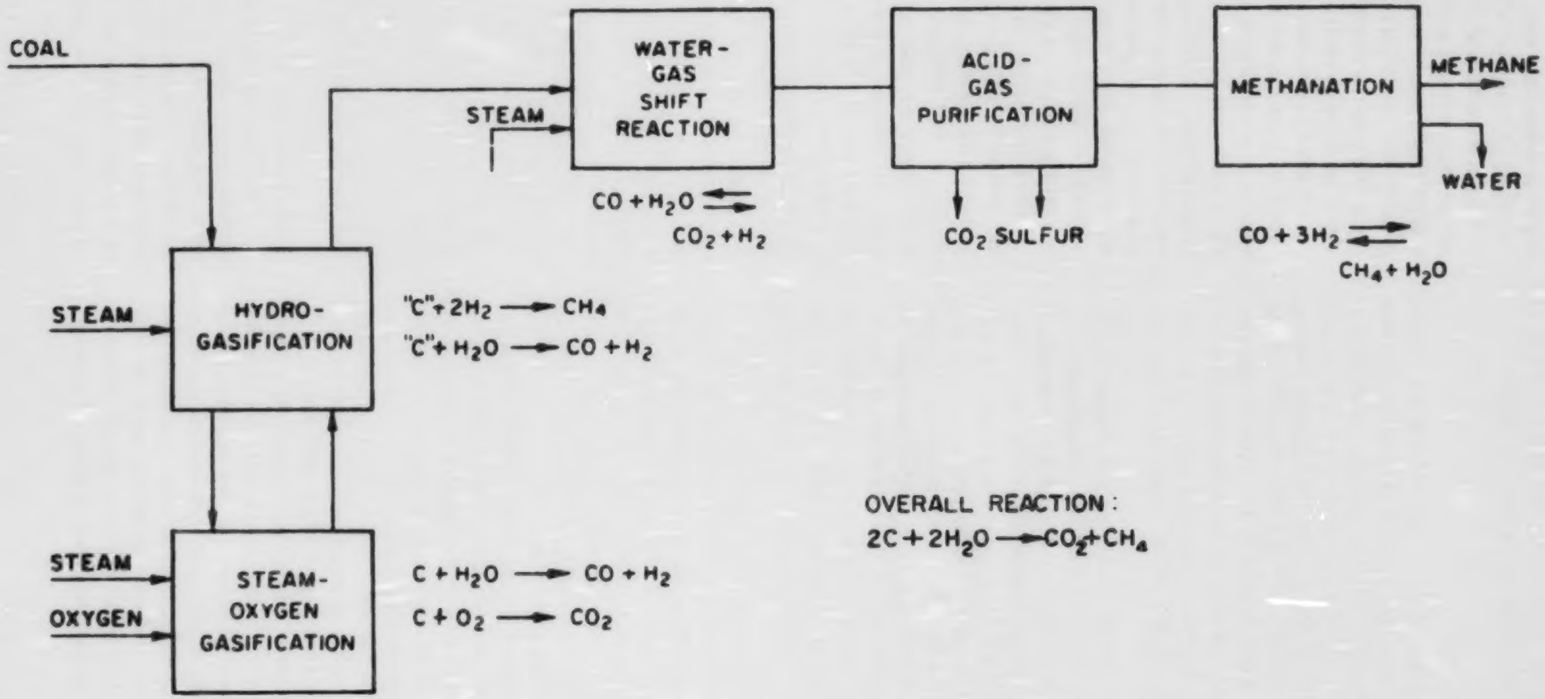

COAL
STEAM
STEAM
OXYGEN
HYDRO-GASIFICATION
STEAM-OXYGEN GASIFICATION
"C"+ 2H2 → CH4
"C"+ H2O → CO + H2
C + H2O → CO + H2
C + O2 → CO2
STEAM
WATER-GAS SHIFT REACTION
CO + H2O ⇄ CO2 + H2
ACID-GAS PURIFICATION
CO2 SULFUR
METHANATION
METHANE
WATER
CO + 3H2 ⇄ CH4 + H2O
OVERALL REACTION:
2C + 2H2O → CO2 + CH4

Figure 5. Pipeline gas production using hydrogasification.

Claus plant tail-gas cleanup, this standard may be thermodynamically impossible under many conditions.

Carbon Dioxide Vent

As indicated earlier in the chemistry of coal conversion, the quantity of carbon dioxide that must be vented from the coal gasification complex must be even greater than the quantity of methane that is produced. For a second generation process, the CO_2-rich vent gas will total 275 to 300 x 10^6 SCF/day for a 250 million cu ft/day gas output. Because of the higher oxygen consumption in processes utilizing the older technology, the carbon dioxide formation increases and we have seen designs with up to 400 million SCF/day of CO_2 discharged.

This carbon dioxide cannot be pure. Present separation technology indicates that small concentrations of other materials must be present in the gas. In particular, the separation between some species of sulfur compounds and carbon dioxide cannot be perfect; a significant fraction of the organic sulfur species present in the raw off-gas will be discharged with the carbon dioxide. Our inquiries indicate that most gasifier developers do not have hard data on the concentrations of organic sulfur species in the raw off-gas, nor do they know if it will be converted to hydrogen sulfide (for easier removal) during the processing prior to the sulfur and CO_2 removal steps. Our "calculational" studies, based upon inputs from acid-gas removal licensors, indicate that perhaps 1-4 percent of all sulfur in the gasifier feed may appear in the CO_2 off-gas (based only upon theoretical considerations). Practically, the losses might be higher. However, we understand that a recent study for EPA indicated that this sulfur, primarily in the form of carbonyl sulfide, is a relatively preferred sulfur species because it is odorless and noncorrosive.

The raw product gas will also contain hydrogen, carbon monoxide, as well as hydrocarbons — some of these must also be lost with the carbon dioxide because, again, the separation cannot be perfect. The expected hydrogen and carbon monoxide concentrations will be low (although the tonnages may be significant because the total CO_2 release is large), but the potential for hydrocarbon emissions causes the greatest concern. It is here that we pay some penalty for the improved efficiencies discussed earlier. If the process were not designed for direct methane formation, no hydrocarbons would exist in this gas stream and hydrocarbon emissions would be a moot point. However, when we design the gasifier for direct methane formation, some of that methane will be lost with the carbon dioxide. Additionally, when we design for direct methane formation, higher hydrocarbons may be present in the gas stream and some of these will also be lost. In particular, if C_2 and C_3 hydrocarbons are present, the processes that now appear most economical for acid-gas removal will show a relatively high loss of these hydrocarbons to the carbon dioxide vent gas. We have seen flowsheets that indicate up to 200 tons/day of methane or ethane will be present in this gas stream, as indicated in table 1.

Of even greater importance is the potential for discharge of nonsaturated hydrocarbons. Some processes tend to generate olefins such as ethylene or propylene. These species are active in the photochemical oxidation cycle and they will be largely lost to the carbon dioxide vent from the system. We at IGT know that the olefin production in our gasifier is much less than has been estimated for other systems, but we do not yet have sufficient operating experience on the pilot plant to define the scale-up production rates for these species.

Some engineering companies have operated under the philosophy of incineration of any vent stream that contains hydrocarbons. We believe this philosophy is unrealistic in the necessary compromise between energy supply and environmental protection. In one plant design, the energy required for incineration of the CO_2-vent gas was 1000 million Btu/hr. If this quantity of energy were taken from the product gas, 10 percent of the plant output would be consumed for incineration. This is enough energy to supply the average fuel requirements for 65,000 homes—or the total residential energy requirements of a city of one-quarter million. If feedstock coal is used for the incineration, the incineration fuel requirement is 25-33 percent of the boiler house fuel requirement, with a resulting similar increase in emissions of SO_2, NO_X, and particulates.

Defining a reasonable loss of hydrocarbons to this vent gas is difficult. We believe that guidelines cannot be realistically defined until the first of these facilities have been demonstrated and hard, steady-state data are collected on quantities and composition of hydrocarbon losses. Further, the quantities and types of emissions from developing processes will be different from those from older technology and each system must be carefully weighed on a cost-benefit analysis.

Solid Waste Discharge

The flowsheet of figure 2 indicates a single solids disposal system comprised of wastes from three major areas — gasifier and boiler house ash, calcium sulfite-sulfate sludge from stack-gas scrubbing, and sludges from both raw water and wastewater treatment. Of these various solids streams, the gasifier developer has a major influence on only the gasifier ash and perhaps a minor effect upon the sludge from wastewater treatment. The waste solids from sources other than the gasifier and the wastewater have been handled elsewhere and no new problems are anticipated. For that matter, the additional gasifier ash may help eliminate the usual problems encountered with lime sludge disposal. The sludge from wastewater treatment is a function of the gasifier type and the treatment processing used; it will be discussed in the next subsection.

The ash from the gasifier can exist in many forms, depending upon the characteristics of the coal feedstock and the operating conditions within the gasifier. In some cases, this ash will resemble fly ash; in others, the ash will be a slag. In one of our gasifier configurations, the ash is a nearly white (or red if the coal contained significant pyrite) powder; in another configuration, the ash resembles small, round, hard pellets. We do not anticipate that significant environmental hazards will be found with the ash because it is the solid material that remains after extreme treatment. Nevertheless, we do not yet have hard, long-term data to confirm or deny this hypothesis.

The only published results that we have seen on this subject are studies by Peabody Coal Company on ash produced at the Westfield tests. The results of that work indicated that gasifier ash could be satisfactorily disposed of in worked-out sections of the original coal mine.

Wastewater

A foul water stream will be generated in most gasification processes. This stream will result from the quenching and water-washing of the raw gas to remove water-soluble impurities such as ammonia, H_2S, and phenols. The characteristics of this foul water will be functions of the raw coal composition, the gasifier design, and the techniques that are used for quenching and washing the raw gas.

The nitrogen content of the raw coal is expected to be largely converted to ammonia in many gasifiers. Some configurations will tend to produce small quantities of cyanide as well. Much of this cyanide is further converted to thiocyanates in the quench water. Coals with high oxygen content tend to produce phenolic compounds that may appear in the wash water. Most of the chlorine in the coal will be gasified to chlorides and will also appear in the water.

Some gasifier configurations tend to convert a significant proportion of the coal into tars and heavy oils. Depending upon the configuration of the quench system, some of these higher organic compounds may be emulsified into the wash water. In our own high-Btu gasification system, tars are not produced and heavier aromatic compounds can be recycled to extinction with little contact with quench water.

Figure 6 presents a possible water reuse plan for a hypothetical coal gasification facility. For this 250 million SCF/day plant, we have assumed 6000 gpm of raw water as typical of a water-conservation plant that maximizes air cooling. Consumption of water into the product is 1330 gpm and the cooling tower evaporation is 3820 gpm. The total net foul water make is 1570 gpm.

If the quantity of phenols made in the gasifier were high, recovery of the phenols from the foul water would be economical. A liquid-extraction system would recover most of the phenols and other organic impurities from the foul water for byproduct credit. This box is shown in dashed lines on figure 6 because this recovery is not necessarily economic with all gasifier types and coals.

The next step in foul water treatment is stripping for recovery of ammonia and elimination of H_2S and CO_2 that dissolved with the ammonia. The ammonia is recovered for byproduct value and the acid-gases would be directed to the Claus plant for sulfur recovery.

The next step shown in figure 6 is biological oxidation. If phenol recovery is not practiced, this bi-ox stage is necessary for destruction of organic matter. If phenol recovery were practiced, the bi-ox could perhaps be shifted to the smaller, cooling tower blowdown stream. The waste solids sludge from the biological oxidation will be a function of the impurities present in the foul liquor and the degree of pretreatment before the sludge is produced. Note also that biological oxidation is not the only alternative for this purification. Pressure thermal oxidation may be considered and secondary treatment, such as ozonation, chlorination, or oxygen treatment, may be the better route.

The treated foul water now has sufficient purity that it may be injected into the cooling water circuit, together with treated raw water. We have assumed a net cooling tower blowdown of 900 gpm for this facility. This blowdown will contain the water-soluble compounds that were not removed earlier. These include chlorides, perhaps as ammonium chloride, and a portion of the thiocyanates may still be present.

We have shown a dotted box for concentration as the next step in the water management. If the design philosophy of the facility is no water discharge, the engineer may use excess low-pressure steam from the process to concentrate this blowdown stream by a factor of about 6. The concentrated blowdown would then be used for ash quenching within the gasifier (with resultant steam make into the gasifier) and the final discharged ash would contain small quantities of water. Under this philosophy, the ash will contain all of the water-soluble material in the cooling tower blowdown, including the

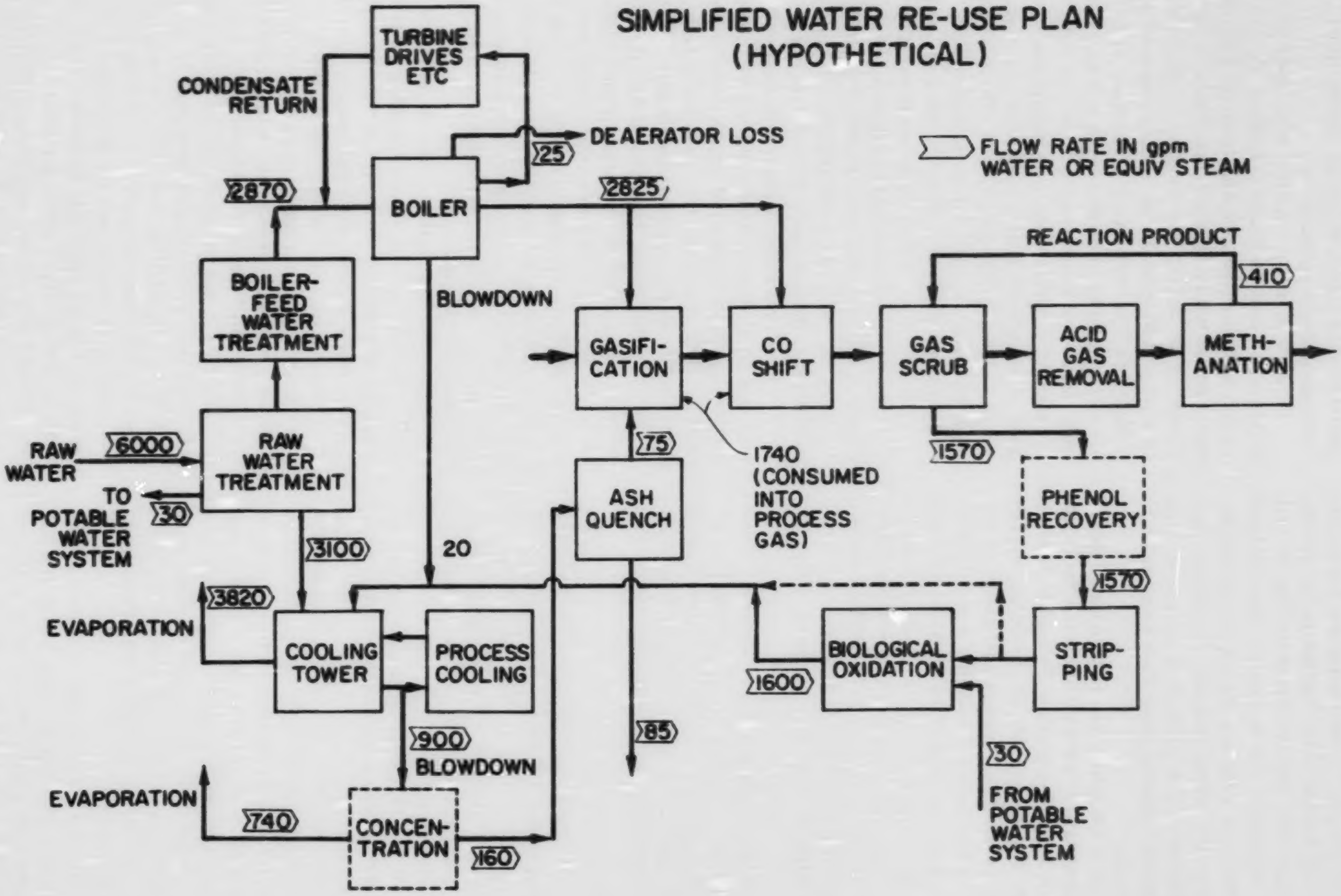

SIMPLIFIED WATER RE-USE PLAN
(HYPOTHETICAL)
FLOW RATE IN gpm WATER OR EQUIV STEAM
TURBINE DRIVES ETC
CONDENSATE RETURN
DEAERATOR LOSS
25
2870
BOILER
2825
BOILER-FEED WATER TREATMENT
BLOWDOWN
REACTION PRODUCT
410
GASIFI-CATION
CO SHIFT
GAS SCRUB
ACID GAS REMOVAL
METH-ANATION
RAW WATER
6000
RAW WATER TREATMENT
TO POTABLE WATER SYSTEM
30
75
1740 (CONSUMED INTO PROCESS GAS)
1570
ASH QUENCH
PHENOL RECOVERY
3100
20
1570
3820
EVAPORATION
COOLING TOWER
PROCESS COOLING
BIOLOGICAL OXIDATION
STRIP-PING
1600
900
BLOWDOWN
85
30
FROM POTABLE WATER SYSTEM
EVAPORATION
740
CONCEN-TRATION
160

Figure 6. Simplified water re-use plan (hypothetical)

chlorides of the coal and salts present in the raw water. Therefore, under this philosophy, the ash would be subject to leaching.

The alternative solution is to either evaporate the cooling tower blowdown to dryness, generating a small, water-soluble solids stream, or develop disposal techniques for a waste liquid.

At present, we can only estimate the characteristics of this waste. We do not have hard data on the contaminants present in the foul water as a function of coal feedstock, gasifier operating conditions, and method of gas quenching and washing. Further, we do not have quantitative data on the fate of potential pollutants as this foul water passes through the various purification stages. Data from a pilot plant are not necessarily applicable because the engineering design of a commercial facility may use different gas processing and water treatment techniques. In short, the quantities and compositions of water-soluble materials that may be present as a final waste from a coal gasification facility cannot now be predicted with accuracy.

SUMMARY

Coal gasification appears to be an environmentally and economically preferred alternative for the generation of clean fuel from coal to meet residential demands. The gasifier developer has the maximum impact upon emissions from the overall plant in the areas of boiler-house emissions and characteristics of the discharged ash. The gasifier will have a lesser impact upon the quantities of potential pollutants in the discharged carbon dioxide stream and wastewater; the plant design engineer will have a greater effect on these streams and the maximum effect on other potential discharges.

At present, there are data gaps in several areas of environmental concern; we anticipate that funding will soon be available to enable us to attack these gaps. With additional pilot plant development work, we believe that the environmental effects for large-scale plants can be estimated with better accuracy than is now possible. The environmentally related purpose of pilot plant operation is to develop data on the raw products of the gasifier as functions of the operating variables and coal feedstocks, acquiring basic data for the design engineers. However, the short-term pilot-plant operations, even with engineering evaluation, cannot provide a hard basis for defining future environmental discharges — there are simply too many unknown factors and variables to allow precise predictions of large-scale performance on the basis of pilot plant testing. Rather, the measurement of the overall system discharges must await the construction and operation of large-scale, continuously-operated plants, to evaluate the effectiveness of proposed engineering solutions to environmental control problems.

BIGAS PROCESS*

V. D. Kliewer and V. L. Brant†

Abstract

Construction of a plant to pilot the BIGAS Coal Gasification Process is nearing completion. This plant is a grass roots plant processing coal through a Coal Preparation Unit and Gasifier, and carrying the gas through shift *and* methanation, *producing a high Btu fuel gas product. An advantage of this process is the flexibility of the gasifier in that it could be made to handle many feed stocks and the relatively high yield of methane produced when directly gasifying coal. Where foreseeable in this new process, facilities have been provided to handle vapor emissions and liquid effluents, and to produce a sweet gas. Actual operation will provide more knowledge on solving environmental problems of BIGAS plants.*

Several years ago, Bituminous Coal Research, Incorporated, located in Monroeville, Pennsylvania, undertook the development of a new coal gasification process. This new process is now referred to as the BIGAS Process. Development work by BCR proceeded from batch type experiments through continuous flow experiments in a 5 lb/hr externally heated reactor to operation of a 100 lb/hr internally fired, Stage II, Process Equipment Development Unit. Using the correlations obtained in the Stage II test program, Stearns-Roger, Incorporated, performed the detailed engineering and construction of a pilot plant. That pilot plant is located in Homer City, Pennsylvania and is almost ready to go onstream. Equipment shakedown is now in progress. Management for the BIGAS Research Program at the plant is under the direction of the Phillips Petroleum Company of Bartlesville, Oklahoma. Stearns-Roger, Incorporated, will operate the plant.

This plant is a part of the high Btu gas development program supported by the Energy Research and Development Administration and the American Gas Association.

Well, so much for history. I recall from my school days that I never did too well in history; therefore, I must turn to the real subject of this presentation which is the BIGAS Process itself. Many of you, I am sure, are familiar with the process as it has been the subject of several presentations at various technical meetings and references to it have been made in several publications. On the other hand, I suppose that some of you may not be familiar with the process. This afternoon, I would like to briefly discuss the process, point out its current status, and briefly review some environmental aspects and advantages of the process.

Now those who are more professional at speaking than I will undoubtedly say that it is too much subject to cover in the brief period that I have. They may be right. However, to cover the background of many of you who are here, I feel that I must cover this broad a subject. Please bear with me if I get into too much detail in one case or not enough in another. We will allow some time later for questions.

The pilot plant is designed to process 5 tons/hr of coal. Figure 1 is a Generalized Block Flow Diagram of the plant. The plant is a grass roots plant handling coal beginning with feed preparation, through gasification, and ultimately to a methanation unit where pipeline quality gas having a heating value of about 940 Btu/cubic foot is produced. The greatest quantity of byproducts is slag and sulfur.

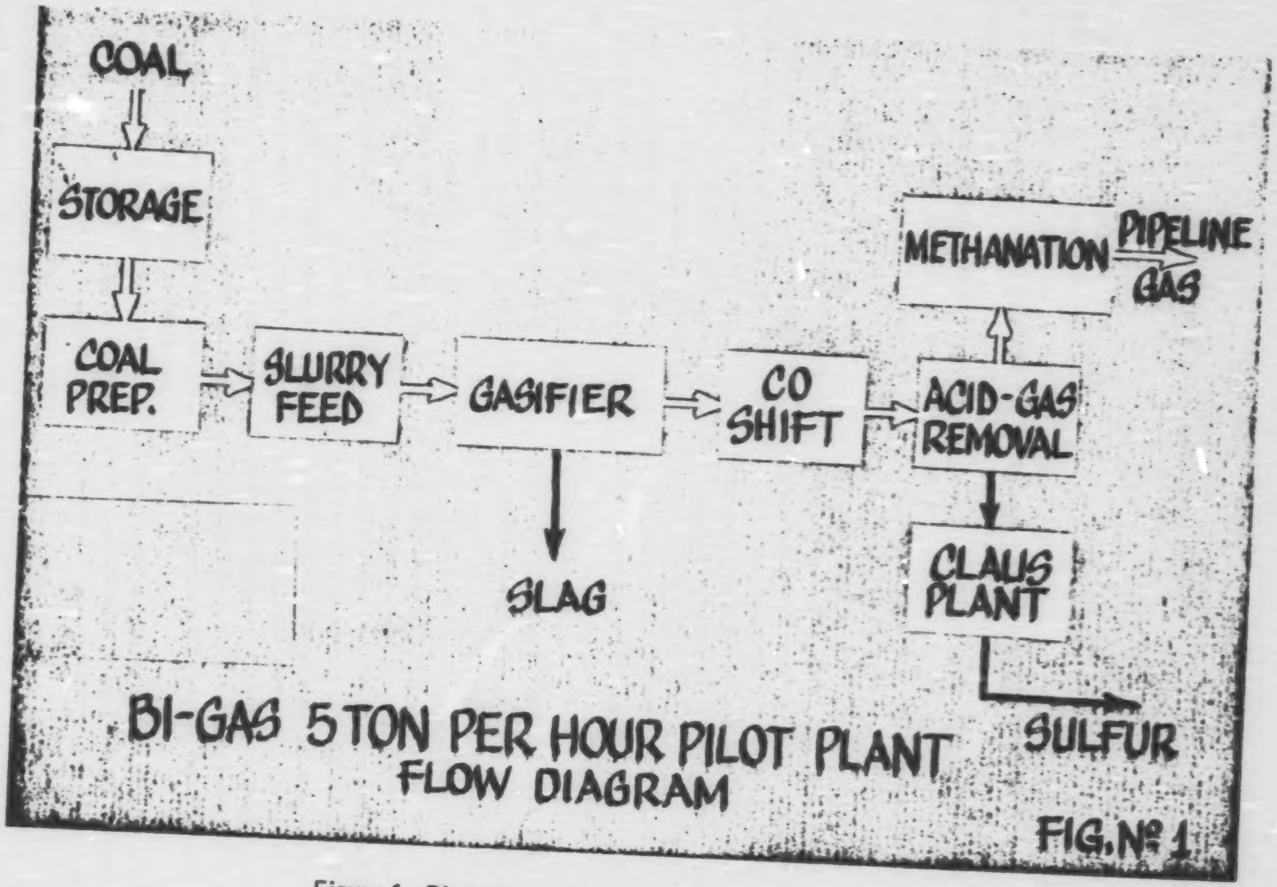
Figure 2 shows the Coal Preparation Section. Coal which will be received by the pilot plant is 1½ inch by zero size. It will be unloaded into large storage bins for feed into the unit. However, about a 14-day supply will be stockpiled outside. Briefly, the function of coal preparation section is to prepare coal for feed to the gasifier by pulverizing it to approximately 70% minus 200 mesh. The coal is wet ground and concentrated into a cake of approximately 50-65% solids. The cake is then slurried with water to the consistency used in the process.

The High Pressure Slurry Feeding System is represented in figure 3. Looking at the lower left, slurry of the proper consistency from the blend tank shown in the previous figure is received by the high pressure slurry pumps. These pumps discharge the slurry at the high pressure required for the reaction. The slurry is fed to a spray drier where all of the water is vaporized. Then the stream is taken to a cyclone where the coal and vapors are separated. The coal is fed by gravity to the gasifier. The vapors from the cyclone are scrubbed, the water condensed, and the vapors heated and returned to the spray drier to vaporize the water in the slurry. There are no environmental problems associated with this section of the plant. The inert gas vapors carrying heat to the

---

*This paper is based on work carried out by Bituminous Coal Research, Inc. and Stearns-Roger, Inc., with support from the Energy Research and Development Administration under contract E(49-18)-1207 and the American Gas Association.

†V. D. Kliewer and V. L. Brant are with Stearns-Roger, Incorporated, Box 5888, Denver, Colorado 80217.



COAL
STORAGE
COAL PREP.
SLURRY FEED
GASIFIER
SLAG
CO SHIFT
ACID-GAS REMOVAL
METHANATION
PIPELINE GAS
CLAUS PLANT
SULFUR
BI-GAS 5 TON PER HOUR PILOT PLANT FLOW DIAGRAM

FIG. Nº 1

Figure 1. Bigas 5 ton per hour pilot plant flow diagram.

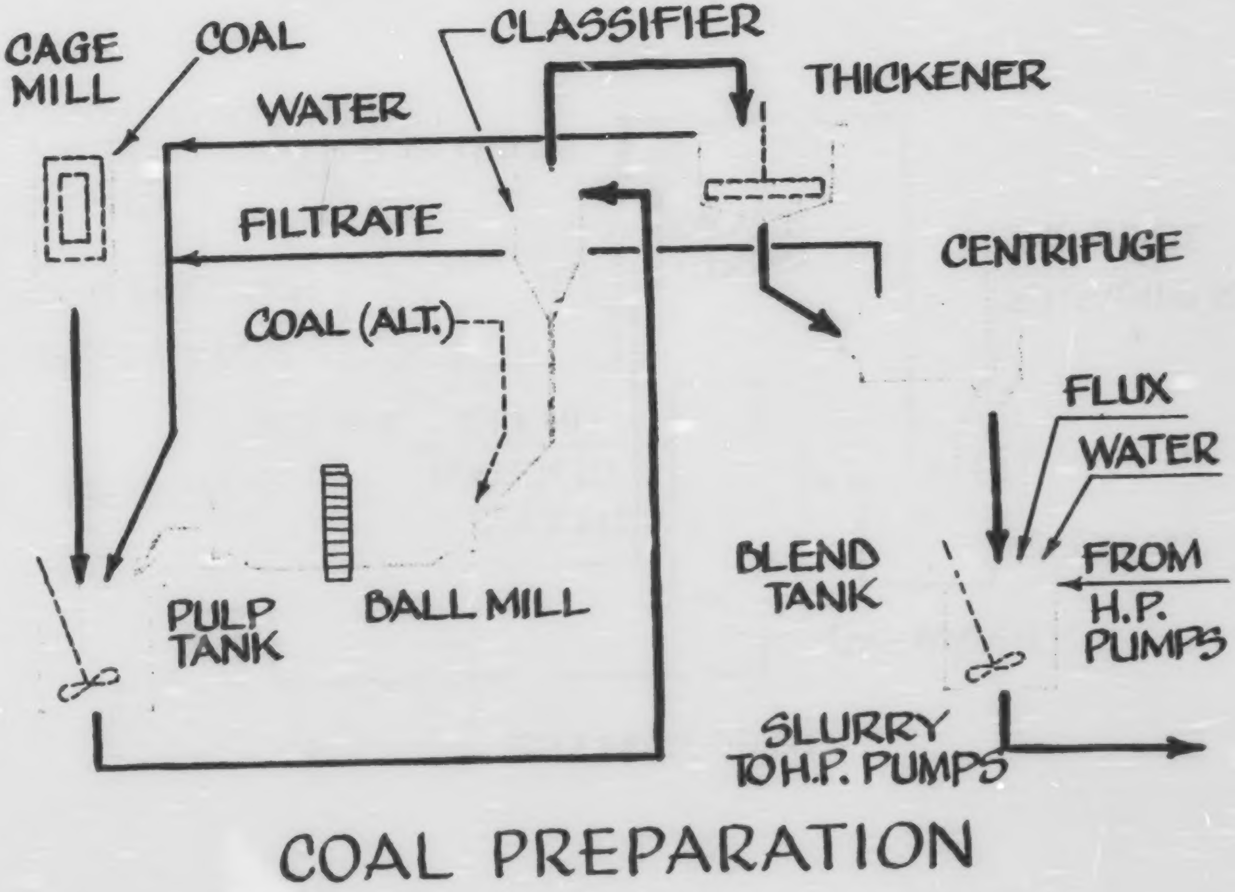

CAGE MILL
COAL
WATER
FILTRATE
COAL (ALT.)
CLASSIFIER
THICKENER
CENTRIFUGE
PULP TANK
BALL MILL
BLEND TANK
FLUX
WATER
FROM H.P. PUMPS
SLURRY TO H.P. PUMPS
COAL PREPARATION

Figure 2. Coal preparation.

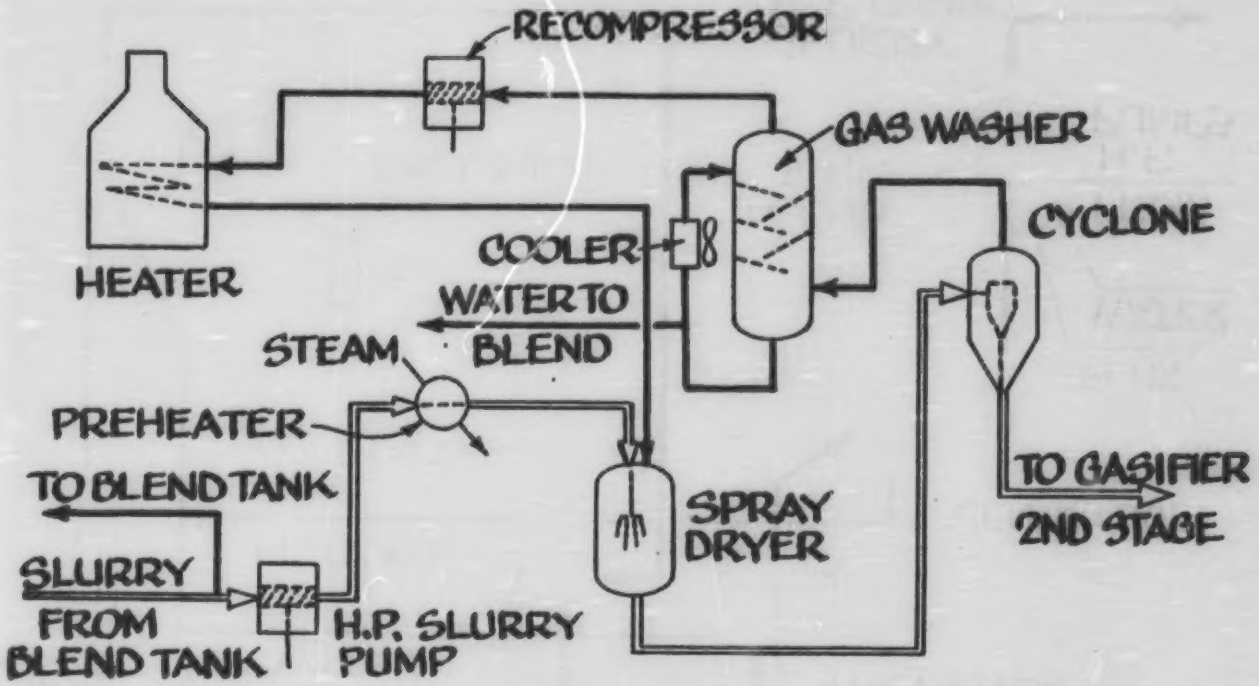

RECOMPRESSOR
GAS WASHER
CYCLONE
HEATER
COOLER
WATER TO BLEND
STEAM
PREHEATER
TO BLEND TANK
SLURRY FROM BLEND TANK
H.P. SLURRY PUMP
SPRAY DRYER
TO GASIFIER 2ND STAGE

Figure 3. High-pressure slurry feed system.

spray drier are in a captive system and are not released. The water from the gas washer is returned to the feed preparation section to slurry the coal and is also not released.

The heart of the BIGAS Process is the two-stage gasifier shown schematically in figure 4. The gasifier has three defined sections: Stage II at the top; Stage I in the middle; and the Slag Quench Zone. Each section is separated by formed restrictions. The gasifier processes pulverized coal in entrained flow. On the left side of the figure, coal from the cyclone is fluidized by recycle gas and conveyed into Stage II of the gasifier. Steam is also introduced at the same point. There, they combine with the rising hot synthesis gas from Stage I. The mixing temperature of about 2200° F is rapidly attained and the coal is converted to methane, synthesis gas, and char. This raw gas and char are carried overhead from the gasifier at about 1700° F. Char in the raw gas is separated in a cyclone and returned to Stage I of the Gasifier. Steam required for the reaction carries the char into the Gasifier. Oxygen is fed through a separate injector and combines with the char in Stage I. The reaction temperature reaches 2700° F to 3000° F and the char is gasified under slagging conditions. The synthesis gas produced along with any unreacted char pass through the throat into the second stage.

The Slag Removal System is shown in figure 5. Molten slag is deposited on the walls of Stage I and flows out the slag tap opening in the bottom of the conical section. The molten slag drops into a reservoir of water in the bottom of the gasifier for rapid quenching where the slag is solidified, and shatters into small pieces. The slag falls through the water and exits the bottom of the gasifier, assisted by the recirculating water. The slag falls into lockhoppers and is ultimately taken as a slurry to a settling pond. The recirculating water is cooled and returned to the gasifier. A slip stream is taken from the Recirculating Water System to the settling pond for fines removal. Clarified water from the settling pond is reused for filling the slag lockhoppers and for dust and fume scrubbing as needed.

Figure 6 shows the Raw Gas Cleanup System. The raw gas leaving the char cyclone passes through a water wash column, where the gas if further cooled and dust is removed. The recirculating water is cooled and returned to the wash tower. Fresh water is added as needed to remove solids. Purged water is sent to the disposal pond.

The remainder of the process steps are listed in figure 7. The clean raw gas is partially shifted to provide the proper H_2/CO ratio. It is important to note that the Shift Unit is also designed to convert all sulfur compounds—such as carbonyl sulfide and carbon desulfide, to hydrogen sulfide. Thus, no processing nor disposal problem associated with these carbon sulfides exists. Hydrogen sulfide and carbon dioxide are removed selectively from the entire gas unit in a SELEXOL Unit. The H_2S is then converted to sulfur product in a Claus Unit. The shifted gas is sent to a methanation unit, then returned to the SELEXOL Unit for final CO_2 removal to produce the high Btu pipeline gas.

Figure 8 is a picture of the plant. The plant site is located approximately 2 miles north of Homer City, Pennsylvania. The site is bounded by Two Lick Creek on the west and north, a coal company on the east, and an industrial part to the south. As you can see, the plant is virtually complete with only some insulating and painting remaining. Equipment is being checked out and startup of the utility systems and feed preparation section is anticipated within the next month.

SUMMARY AND CONCLUSIONS

The BIGAS Process, I think, is a good process. I remember my boyhood days when I had to carry coal from the coal room to a furnace and then carry the ashes to the ash pit outside. If the BIGAS Process—and for that matter any coal gasification process, can eliminate that, its got to be a good process. Seriously, the Process offers several advantages. A high yield of methane is obtained directly from coal, thus reducing oxygen consumption and downstream processing. All types of coal can be gasified without prior treatment because the coal is in an entrained system within the gasifier rather than a fixed or fluid bed system. The rapid heating and reaction conditions in Stage II are such that no tars and oils are formed, thus eliminating that problem. The two-stage gasifier, being an integral unit, is relatively simple in design and can be easily scaled-up to larger sizes. The gasifier is also extremely versatile and can accept many feed stocks. Most any carbon containing feed could be processed in the gasifier to produce syngas.

Though heavy sludges are not expected to be formed in this process, it is interesting to note that if there were sludges, a system could be worked out to mix that sludge with the coal slurry and charge it to the gasifier for conversion to syngas.

In the design of the plant, all possible points of emission have been considered and measures taken to mitigate those emissions.

All of the waste water streams in this plant are collected in a disposal pond. In this pond, coal fines from the several fines containing streams will settle out and can ultimately be removed. This process produces a relatively small amount of sour water. However, those waters which are produced are flashed in a low pressure

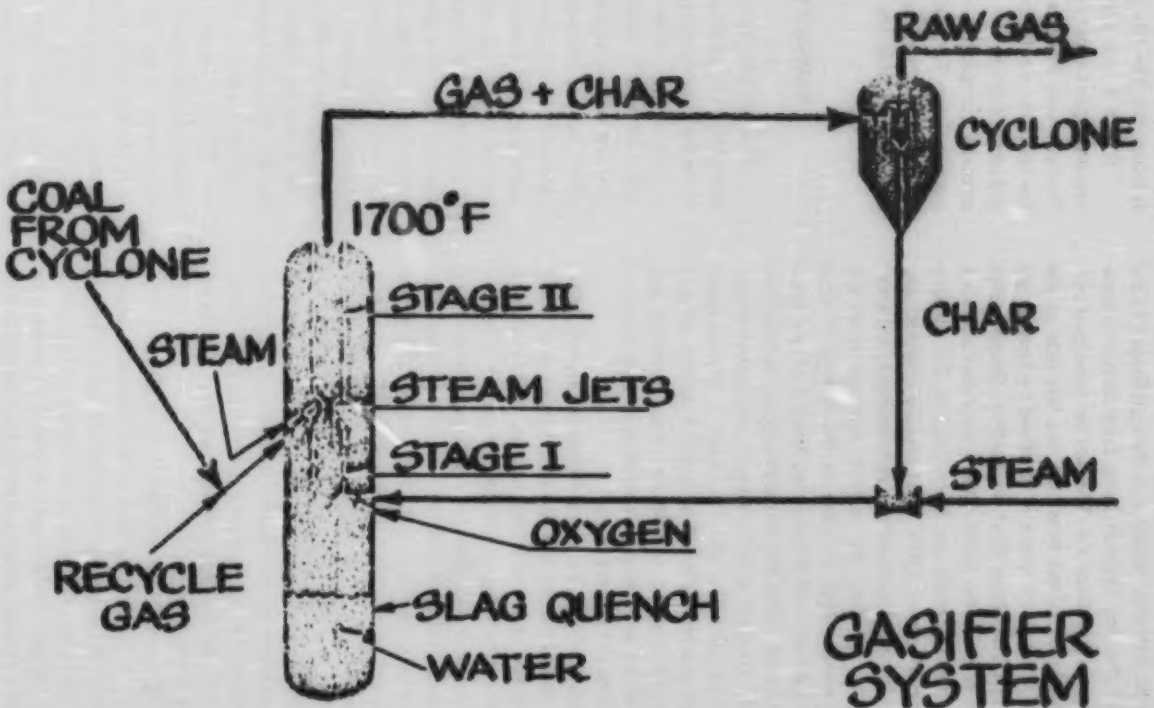

RAW GAS
GAS + CHAR
CYCLONE
COAL FROM CYCLONE
1700°F
STAGE II
STEAM
STEAM JETS
CHAR
STAGE I
STEAM
OXYGEN
RECYCLE GAS
SLAG QUENCH
WATER
GASIFIER SYSTEM

Figure 4. Gasifier system.

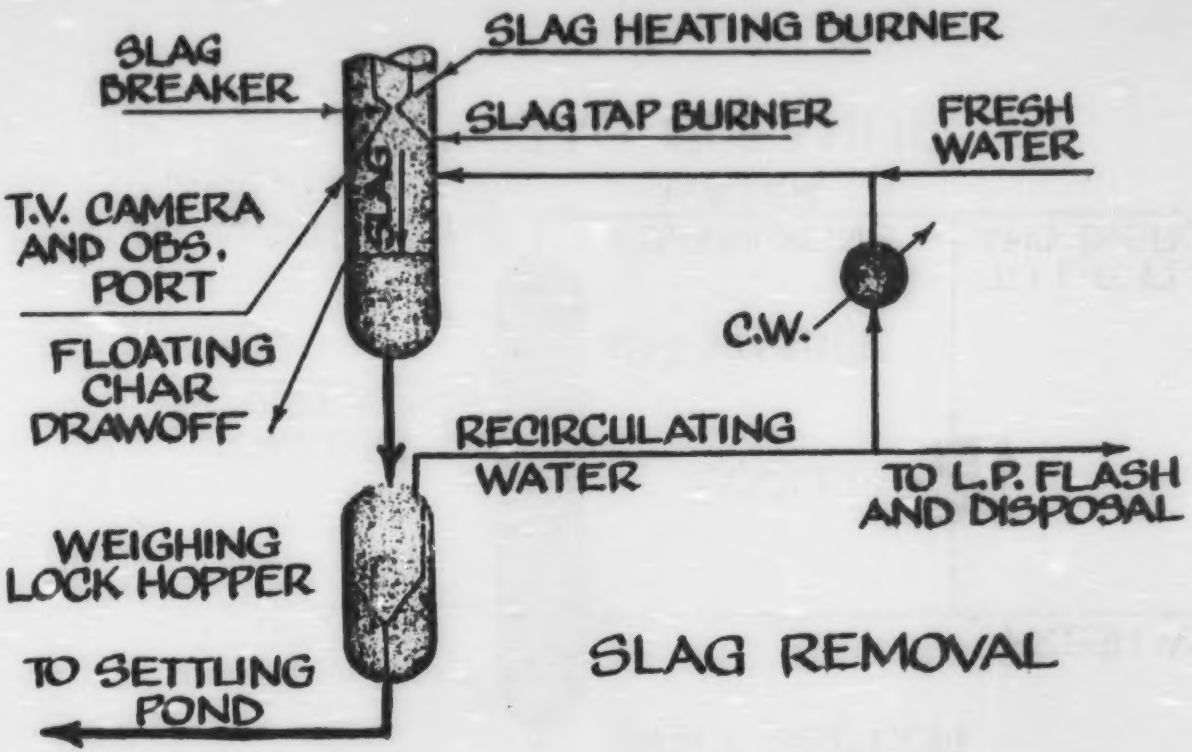

SLAG BREAKER
SLAG HEATING BURNER
SLAG TAP BURNER
FRESH WATER
SLAG
T.V. CAMERA AND OBS. PORT
C.W.
FLOATING CHAR DRAWOFF
RECIRCULATING WATER
TO L.P. FLASH AND DISPOSAL
WEIGHING LOCK HOPPER
TO SETTLING POND
SLAG REMOVAL

Figure 5. Slag removal.

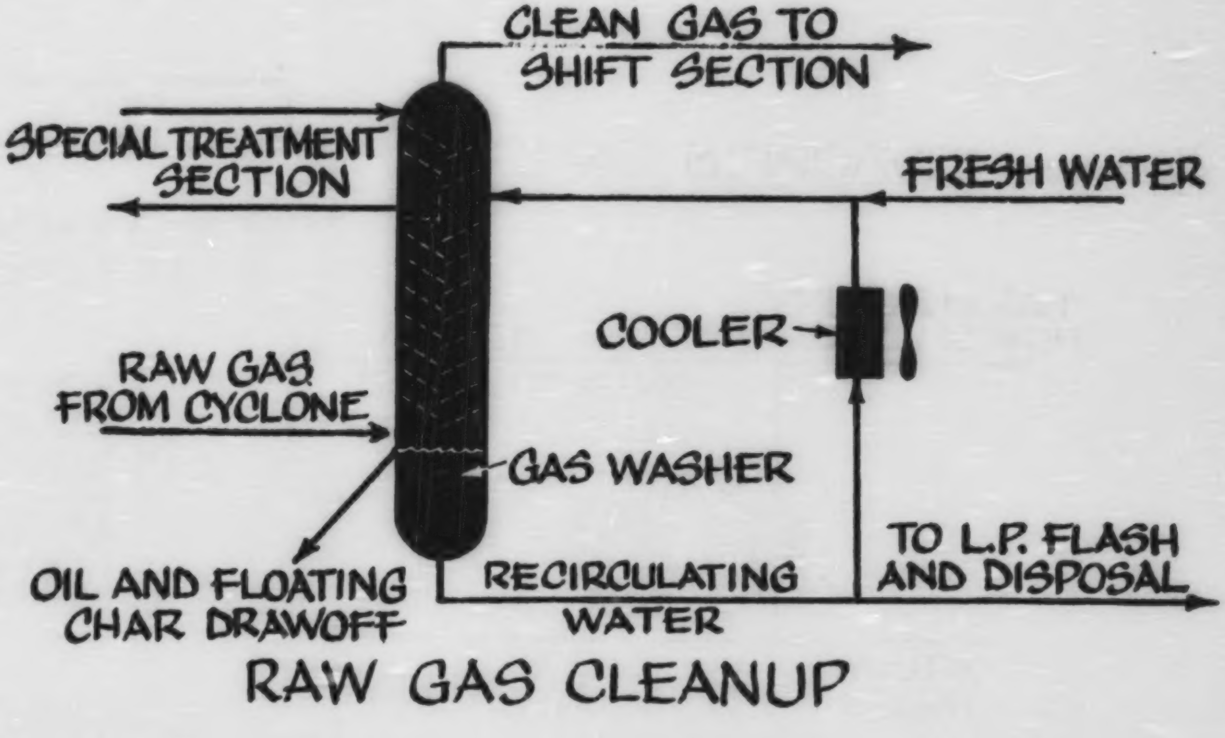

CLEAN GAS TO
SHIFT SECTION
SPECIAL TREATMENT
SECTION
FRESH WATER
COOLER
RAW GAS
FROM CYCLONE
GAS WASHER
TO L.P. FLASH
AND DISPOSAL
OIL AND FLOATING
CHAR DRAWOFF
RECIRCULATING
WATER
RAW GAS CLEANUP

Figure 6. Raw gas cleanup.

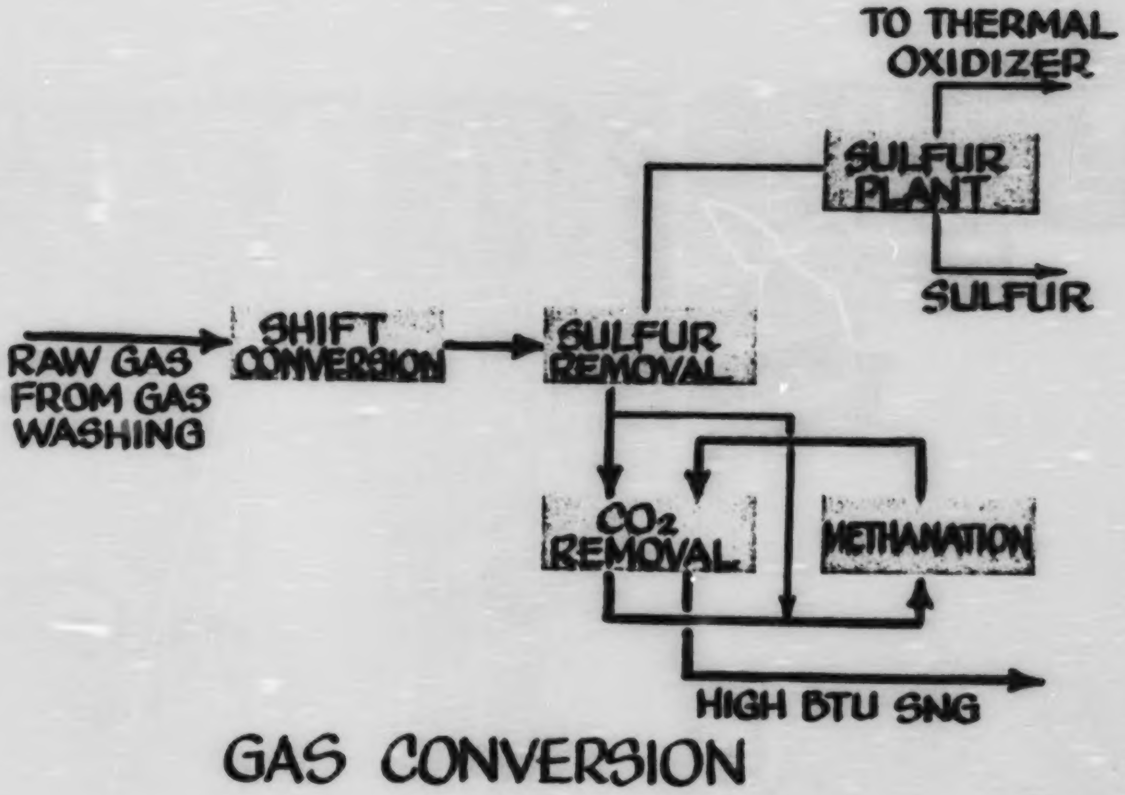

TO THERMAL OXIDIZER
SULFUR PLANT
SULFUR
RAW GAS FROM GAS WASHING
SHIFT CONVERSION
SULFUR REMOVAL
CO2 REMOVAL
METHANATION
HIGH BTU SNG
GAS CONVERSION

Figure 7. Gas conversion.

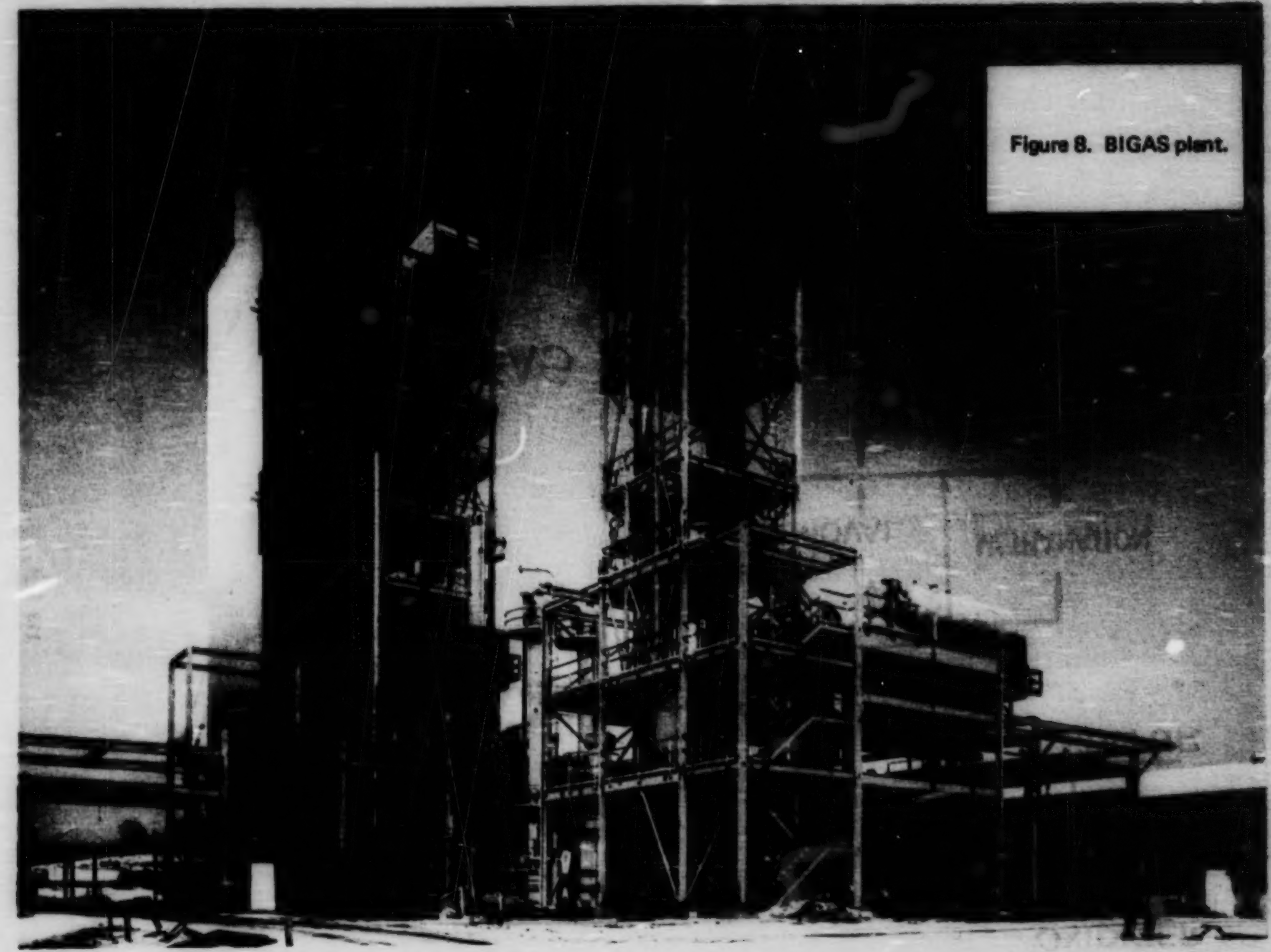


Figure 8. BIGAS plant.

flash drum are disposed of in a thermal oxidizer. The disposal pond itself is concrete, thus there will be no seepage of the waste waters into the ground water system. The waters from the disposal pond are processed in a secondary treatment sewage disposal plant. The coal storage pile itself is inside a curbed area. Rainwater runoff is collected and pumped to the disposal pond.

In the coal preparation section, coal is pulverized in a wet system minimizing dust emissions. Where dry coal is handled, all conveyors are covered and processing occurs in closed vessels or containers where dust can be collected. At points of possible dusting, a dust suppression liquid is sprayed on the coal. Where there may be dust in vent gases, they are passed through bag filters prior to discharge into the atmosphere.

One problem, in my opinion—especially from commercially sized coal gasification units, whether it be the BIGAS Process or other processes, is disposal of the large amount of ash or slag formed. In the BIGAS Process, however, this slag has a glass-like finish and is rather impervious. It is essentially inert and should cause no odor problems.

THE WINKLER PROCESS
A ROUTE TO CLEAN FUEL FROM COAL

I. N. Banchik*

Abstract

The Winkler Process is a fluid bed, coal gasification process and has been in successful commercial service since its discovery by Dr. Fritz Winkler in the early 1920's.

Davy Powergas is currently updating the technology to adapt it to the conditions existing in this country and to make it more economically attractive. This paper describes the technical features of the current version of the process and discusses many of its effects on the environment. In addition, the economics of a large scale fuel gas from coal facility are presented.

The first commercial plant utilizing the Winkler Process was built in 1926 at Leuna, in what is now East Germany and, since that time, 36 gasifiers have operated successfully on a commercial scale. These facilities--all designed, engineered, and commissioned by what is now DPG GmbH, have been used to produce fuel gas and synthesis gas for the production of ammonia, methanol, and gasoline when coal was the only raw material available. To date, a number of these units are still in continuous operation and may be visited, if desired. All of these units have operated at such a pressure as to deliver the gas at 1 psig after cooling and particulate removal; historically, the required gasifier pressure was in the order of 1.5 Atmospheres Absolute.

Several years ago, Davy Powergas undertook an analysis of the applicability of this time-proven Winkler technology to the U.S. market and found that although it was technically sound, changes would have to be made to improve the overall economics of the process. It became rather obvious that the process' greatest deficit was the low pressure of operation since the effects of low pressure are threefold:

1. The large size equipment necessary to handle the large volume of gas.
2. The high capital cost attributable to a gas compression station.
3. The high daily operating cost for the gas compression station.

Proceeding on a course to increase the pressure of operation, laboratory tests were performed to verify that the same fluidization characteristics which are present at atmospheric pressure could be maintained at elevated pressure. In the opinion of the experts, it was expected that at elevated pressures the thermodynamics and kinetics of the process would be as good or better than at atmospheric pressure; hence, an analysis of the mechanics of operating a Winkler system under pressure was begun. It was found that there are available several commercially proven pressurized feed systems operating under similar conditions, i.e., pressure blast furnaces, Lurgi gasifiers, etc., and these form the basis for the design of the pressurized Winkler system described below.

A unit designed to produce fuel gas from coal is shown in simplified form in figure 1. The plant may be divided into the following operations: (1) coal preparation, (2) gasification and char handling, (3) compression, (4) desulfurization, and (5) sulfur recovery.

Coal Preparation

The feed preparation section can include any or all of the following: crushing to the required size, drying, and transfer to the low pressure feed bunkers. Normally, the drying step is only required if surface moisture exists on the coal such that plugging of bins and conveyors will occur; indications are that this level may exceed 30% with some lignites. So long as the coal is surface dry, the decision as to whether to dry will be made on a purely economic basis.

Run of pile coal from the storage pile is conveyed to the cage mill crushers where the particle size is reduced to 3/8" x 0". If predrying of the coal is deemed necessary, or desirable, fluid bed dryers would be utilized to reduce the moisture content to the desired level. In this unit, hot air-heated by the combustion of coal, is used to fluidize the feed material and provide the heat necessary for drying. Most of the dried coal is removed directly from the fluid bed; however, a portion is entrained in the gases leaving the dryer. This entrained coal, recovered in cyclones, is returned to the dried gasifier feed and conveyed to the gasification section. The hot gases from the cyclone are scrubbed with water for particulate removal prior to disposal.

Gasification and Char Handling (figure 2)

Coal from the low pressure feed bunker passes by means of lock hoppers into the high pressure bunker. At

---

*I. N. Banchik is with Davy Powergas, Inc., Lakeland, Florida.

Preceding page blank

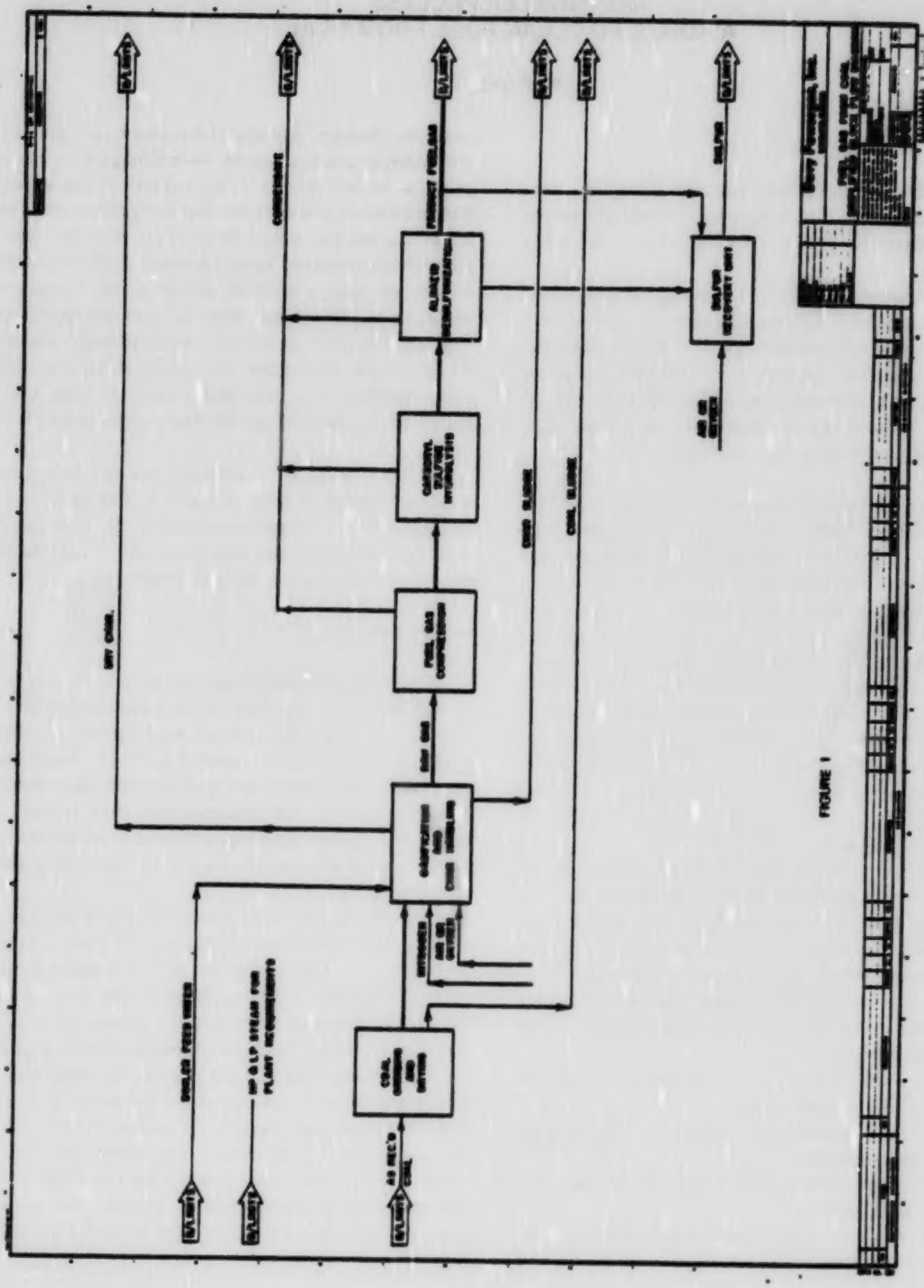

B/LIMITS
DRY CHAR
CONDENSATE
PRODUCT FUELGAS
SULFUR
CHAR SLURRY
COAL SLURRY
ALKAZID DESULFURIZATION
CARBONYL SULFIDE HYDROLYSIS
FUEL GAS COMPRESSION
RAW GAS
SULFUR RECOVERY UNIT
AIR OR OXYGEN
GASIFICATION AND CHAR HANDLING
NITROGEN
AIR OR OXYGEN
BOILER FEED WATER
HP & LP STEAM FOR PLANT REQUIREMENTS
COAL GRINDING AND DRYING
AS REC'D COAL
FIGURE 1

Figure 1. Fuel gas from coal simplified block flow diagram.

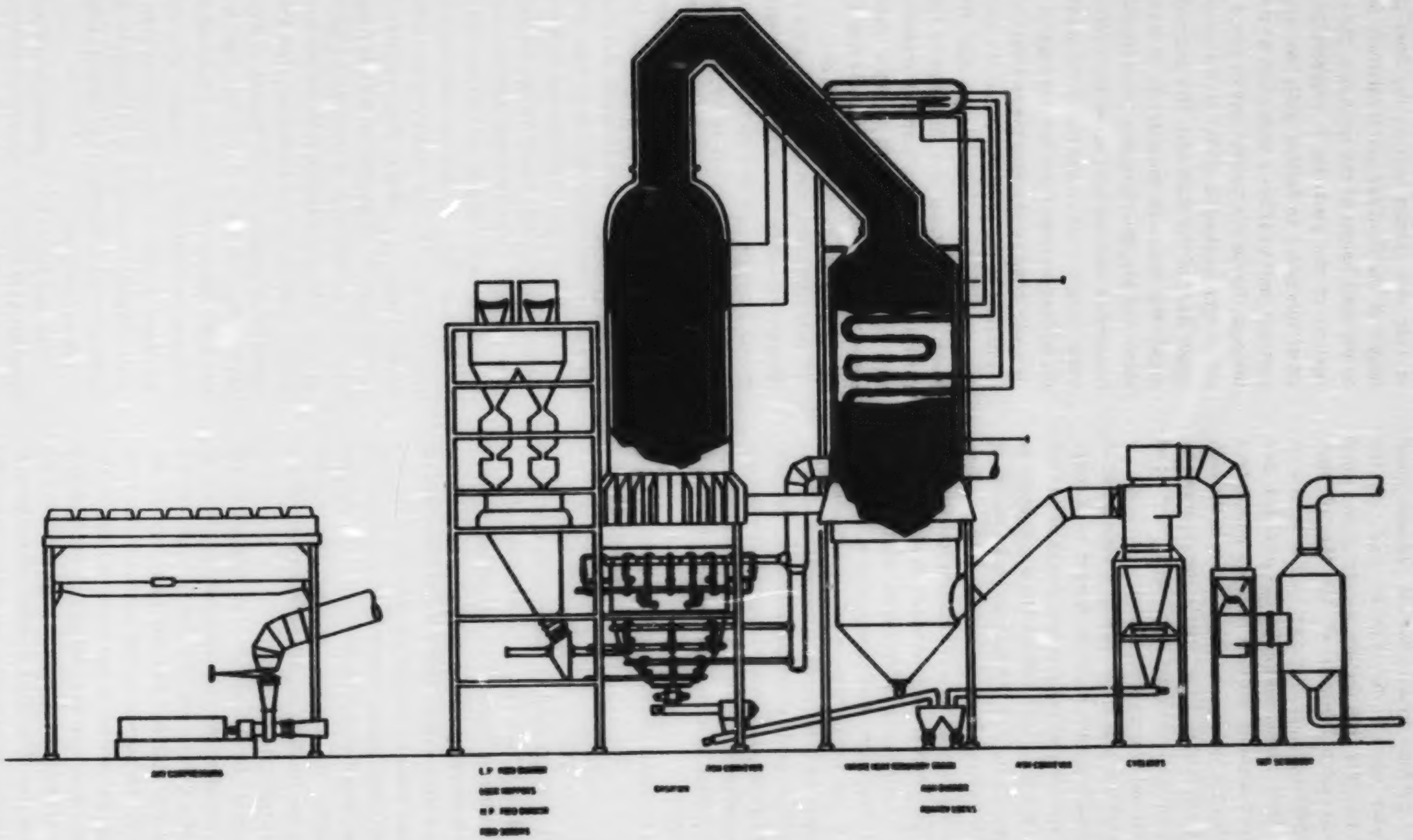


Figure 2. Winkler coal gasifier process schematic.

the bottom of the high pressure bunkers, variable speed screw conveyors control the flow of coal into the Winkler generator. The lock hoppers consist of two small chambers with valves located at the top of each chamber. Depending upon the coal feed rate, two or three parallel lock hopper assemblies are provided: one or two in service and one spare. A nitrogen atmosphere is maintained in the system and the pressure in the high pressure bunker is slightly above that in the generator to prevent the backup of wet gases resulting in plugging of the feed system and generator shutdown.

The bulk of the coal in the gasifier is maintained in a fluid bed operating under pressure. A mixture of steam and air or oxygen is injected at several points within the bed to gasify the coal, while steam alone is injected at the lowest level to fluidize the coal and cool the larger ash particles discharging from the bottom of the gasifier. Air is used as the oxidant when producing low Btu fuel gas while for the production of medium Btu fuel gas, or synthesis gas for ammonia or methanol, oxygen would be required. The high bed temperatures, typically 1700°-2200° F, are obtained by partial combustion of the coal's carbon and contained hydrocarbons. Due to the relatively high gasification temperatures, the tars, gaseous hydrocarbons, and carbon present in the coal are converted to carbon monoxide, hydrogen, and carbon dioxide. Only a small percentage of methane remains in the raw product.

The primary coal gasification reactions are:

$C + O_2 = CO_2$ (exothermic)
$C + \frac{1}{2}O_2 = CO$ (exothermic)
$C + CO_2 = 2CO$ (endothermic)
$C + H_2O = CO + H_2$ (endothermic)
$C + 2H_2O = CO_2 + 2H_2$ (endothermic)

At a constant coal feed rate to the gasifier, the ratio of oxidant and steam to coal is controlled to maintain the desired bed temperature. Optimum bed temperature is a compromise between product gas calorific value, carbon efficiency, and overall thermal efficiency, but is limited by the ash-softening temperature. If this temperature is exceeded, the ash may fuse and agglomerate, thus upsetting the fluidization characteristics of the bed and possibly plugging the reactor.

As a result of the fluidization, the particles of ash and their contained carbon are segregated according to size and specific gravity, i.e., the heavier particles fall down through the fluidized bed and pass into the ash discharge unit at the bottom of the generator while the lighter particles are carried up and out of the bed by the raw product gas. Approximately 50-75% of the incoming ash will be entrained in the hot product gases leaving the top of the generator. The exact quantity entrained with a given gas velocity is primarily dependent upon the particle size distribution in the feed coal. Since the height of the fluidized bed is relatively small compared to the total height of the generator, the upper or major portion of the generator is available to perform two other functions: to further gasify any entrained carbon particles; and to effect a separation of any heavier solid material. To aid this further gasification, a portion of the steam and oxidant is added to the generator near the upper limit of the fluid bed. This secondary gasification causes the maximum temperature to occur in the space above the bed, therefore, any ash particles which may be exposed to temperatures above their softening point are those being carried up and out of the gasifier. To prevent the molten particles from forming deposits on the refractory and possibly blocking the exit duct, a radiant boiler is installed in the generator above the gasification zone. This boiler serves to cool the gas 300°-400° F before it leaves the generator and thus resolidifies any molten particles. The higher gasification temperatures made possible by this feature result in higher gasification efficiencies than were possible previously and also make possible the gasification of less active fuels.

Ash containing hot gases leaving the generator pass through the waste heat recovery train where heat is removed from the gas and particulate by generating the superheating high pressure steam, and preheating boiler feed water. An air preheater may be included to increase the overall thermal efficiency of the process. High pressure steam, thus generated, is normally far in excess of that required by the process and is therefore available to drive steam turbines or for export from the plant.

The heavier char particles leaving the bottom of the gasifier pass through a crusher, exit screw conveyor, and then through a transfer screw conveyor to the ash bunker. The screw conveyors are jacketed for water cooling of the char and a crusher has been included to assure a maximum particle size which will be readily transported in the pneumatic system. The balance of the char is carried out of the gasifier in the overhead product gas. The bulk of this char is removed in the waste heat recovery train and then passes to the ash bunker by means of the transfer screw conveyor. Additional char is removed in a cyclone or multiclones, and reaches the ash bunker in a similar manner, but has its own transfer screw. In combination, the waste heat recovery train and cyclones are designed to remove at least 85% of the entrained solids. From the ash bunker, the char is pneumatically conveyed to a remote location. This material may be disposed of or used as supplemental fuel in a solid fuel boiler.

The gas from the cyclone is scrubbed in a venturi type scrubber to reduce the residual solids to a level of 1 grain/1000 SCF, and a settler is provided to separate the solids from the circulating water loop. Exiting the scrubber, the gases pass through the compression section, if required, and then to desulfurization.

Desulfurization

Removal of the contained sulfur may be accomplished by scrubbing the gas with any of a number of solutions such as amine or hot carbonate. These solutions can be regenerated by stripping to yield a concentrated stream of H_2S and COS, from which the sulfur can be recovered by conventional Claus technology. Alternatively, the H_2S may be converted directly to elemental sulfur in an absorption/oxidation type system such as Stretford. Normally, however, these systems will not remove sulfur compounds other than H_2S. For this particular application, the removal of H_2S and COS to a level of 100 ppm, a combination of carbonyl sulfide hydrolysis and H_2S absorption by Alkazid solution was selected.

Raw product gas from either the scrubber or compression section is heated to reaction temperature and passed to the COS hydrolysis reactor, where the bulk of the carbonyl sulfide reacts with the contained water over a catalyst to form hydrogen sulfide and carbon dioxide. Leaving the reactor, the gas is cooled and sent to the Alkazid absorber.

The alkazid system has been selected for this application as it exhibits a great selectivity for hydrogen sulfide in the presence of carbon dioxide. Therefore, carbon dioxide is not unnecessarily removed, at great energy cost, and a concentrated hydrogen sulfide stream is delivered to the Claus plant for sulfur recovery.

H_2S in the gas is absorbed by lean solution in the absorber and the spent solution is regenerated by steam stripping in a reboiled stripper. The overhead gases from the absorber containing less than 100 ppm of total sulfur are sent to battery limits as product fuel gas.

Sulfur Recovery

Acid gases from the Alkazid regenerator containing approximately 21% by volume hydrogen sulfide are fed to the Claus plant reaction furnace where a portion of the contained sulfur is recovered. Two stages of catalytic conversion are then employed to recover 92% of the sulfur entering the plant as hydrogen sulfide. After removal of the bulk of the elemental sulfur, the gas is sent to an incinerator where all of the residual sulfur and sulfur compounds are oxidized to sulfur dioxide. So that the final effluent gas from this unit is in compliance with air pollution regulations, a Wellman-Lord system has been included to recover the sulfur dioxide and recycle it to the Claus plant inlet. In the event there are other sulfur bearing streams in the plant, i.e., dryer stacks, coal fired boiler stacks, etc., these may be scrubbed in individual absorbers, and all of the sulfur may be recovered in the central chemical plant servicing the Claus plant tailgas.

In the Wellman-Lord system, the gas is contacted with a sulfite rich sodium sulfite-bisulfite solution in a two-stage counterflow absorber. The absorption of sulfur dioxide converts the sulfite in the solution to bisulfite and then the bisulfite rich solution is pumped to the chemical plant for sulfur dioxide recovery. The bisulfite rich solution is fed to a vacuum evaporator where sulfur dioxide and water are driven off resulting in a sulfite rich slurry. The slurry is withdrawn, redissolved in water condensed from the evaporator overhead, and returned to the absorber. Concentrated sulfur dioxide (95 wt.% after water removal) from the evaporator is compressed and recycled to the Claus plant inlet.

An adequate amount of storage is provided for the circulating solution before and after the chemical plant so as to assure continuous operation of the tail gas treating unit even if it should be necessary to shut down the chemical plant for minor repairs and clean outs.

Davy Powergas has recently completed a study to determine the effect of gasifier pressure on the cost to produce low Btu fuel gas from a western subbituminous coal having a heating value of 8640 Btu/lb. The plant being studied had a capacity of 6400 ST/D of coal and delivered the product gas at 210 psig. Capitalization was done on a utility basis, i.e., 65% debt, 35% equity, and the results are shown in figure 3. It is interesting to note that although product gas compression is required in all cases, the optimum pressure for gasification occurs below the desired product gas delivery pressure. It should also be noted that several conservative assumptions were made throughout this study concerning the effect of pressure on gasifier throughput, and it is our opinion that results actually obtained when operating under elevated pressures will be still better than those shown in figure 3.

With respect to the environmental effects of this or any other coal gasification process, it becomes obvious that those plants which had heretofore been built and operated were never erected in what could be considered an environmentally pristine area. In fact, in almost all cases, the effects on the environment are of no concern at all; hence, the lack of detailed information on effluent streams. We recently asked the owners of one of the still operating Winkler facilities for permission to conduct an effluent survey and analysis and permission was denied. The reason for the denial was that if nobody knew what was being emitted from the plant, there could be no legislation against it.

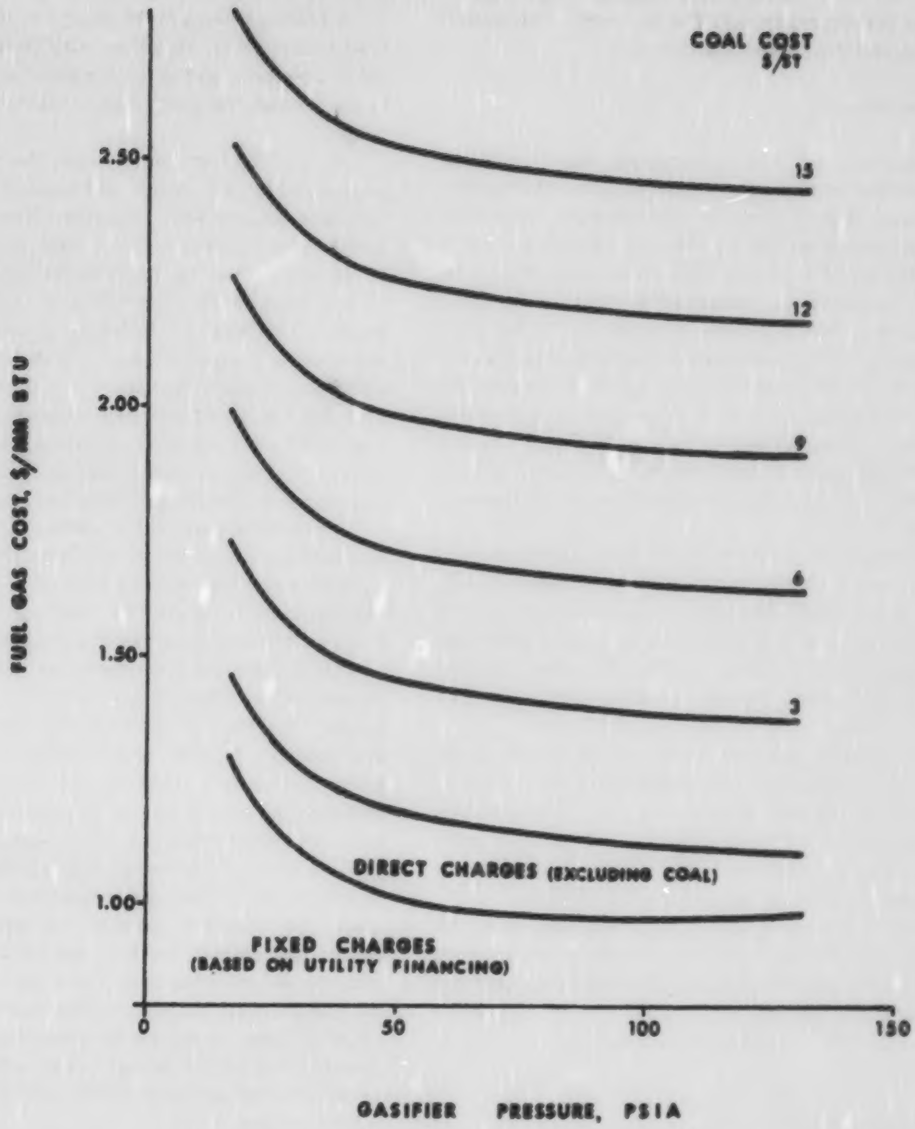


Figure 3. Low But fuel gas from coal by the Winkler process.
Delivery pressure 210 PSIG

Problems attributable to coal piles are common to all processes and, consequently, will be omitted from these discussions. Let it suffice to say that the pile required for this process is relatively small since the process is extremely flexible in both capacity and coal quality. It can be operated on the quality of coal received without the necessity for blending. As an example, when the plant in Kutahya, Turkey began operation, the coal feed contained approximately 20% ash; the current coal supply contains in excess of 40%.

The 3/8" x 0" particle size requirements for Winkler feed eliminates the noise and dust problems normally associated with grinding and also eliminates the fines rejection problem. In some processes, the fines rejected represent 30% of the total plant throughput.

The major effluents from the gasification and char handling section is the char, wet and dry, as the system is enclosed and will contain the dust and gas. Dry char rejected from the system contains unconverted carbon and it therefore would be desirable to recover the heating value by using it as supplemental fuel in a coal fired boiler, as is done at the Winkler unit in Turkey. To do this in the United States would probably require some emission control equipment, but it should be noted that the sulfur level in the char will be far lower than in the raw coal. Although the char exhibits properties of activated carbon, it is relatively inert with respect to the atmosphere and, therefore, could be used as landfill if the carbon loss could be economically tolerated. Dusting of the dry char could be controlled by partial wetting.

Many contaminants normally expected in gases produced from coal such as ammonia, cyanides, etc. would be destroyed, to a large extent, by the high temperature of gasification; and the remainder would probably be adsorbed on the active fly ash as the gas is cooled. Unfortunately, trace element analyses are not available and this subject must be held in abeyance until more data is collected.

Byproduct sulfur produced in the sulfur recovery unit could most probably be sold and thus eliminate the disposal problem; however, depending upon the sulfur removal system selected, there may be small amounts of chemical degradation products to be handled.

The other major effluent problems to be considered are cooling tower blowdown and water treatment plant effluent. Siting of the facility may make the disposal of these streams difficult or easy; but under any circumstances, they must be handled and will be present in almost any chemical or petrochemical plant, irrespective of the raw material.

PRESSURIZED, STIRRED, FIXED-BED GASIFICATION

D. W. Gillmore and A. J. Liberatore*

Abstract

Morgantown Energy Research Center (MERC) of the Energy Research and Development Administration (ERDA) has been operating a 42-inch diameter, pressurized, stirred, fixed-bed gasifier to define operating parameters for various coals and develop technology for commercial scale. Recently, emphasis has been focused on the detailed analysis of gaseous and liquid products and the current program reflects this objective. Some data are reported on the analysis of tar and gaseous constituents.

INTRODUCTION

Morgantown Energy Research Center has been operating a pressurized, stirred, fixed-bed gasifier since 1966, investigating various coals and sizes, and developing technology and hardware for scale-up to commercial size.

Although numerous reports have been issued regarding operating parameters, yields, heat and material balances (refs. 1,2,3,4), little attention has been paid until recently to the minor and trace constituents of the liquid and gaseous products. Plans are laid to investigate extensively the constituents in the raw, cleaned and combusted gases in Fiscal Year 1976. Some data are available now which are worthy of reporting in this environmental symposium.

EXPERIMENTAL

Equipment

The MERC experimental fixed-bed gasifier is a 3.5-foot diameter pressure vessel with provision for stirring deeply within the fuel bed. The fuel bed, 9.6 square feet cross section and a depth of 6-½ feet, is supported on a grate that is rotated continuously. Coal is fed from lock hoppers into the gasifier while ash and cyclone dust are removed by lock hopper systems. Figure 1 shows the entire system.

Air mixed with superheated steam is introduced below the grate and flows upwards through the descending fuel. Gas is withdrawn through an offtake in the top cover which also contains the support and seal for the stirrer. Pressure in the gasifier is developed by the resistance to gas flow through orifices. Two fixed-diameter orifices are used for controlling pressures to 300 psig. A cyclone separator, located between the two orifices, removes most of the dust entrained in the gas. The main gas stream is vented through mufflers and burned in the atmosphere. A small gas flow is diverted from the main stream, cooled, metered, and cleaned of dust, tar, and water before it is analyzed by gas chromatograph for CO, H_2, N_2, CO_2, H_2S, CH_4, C_2H_6, and O_2.

The water-cooled stirrer is supported by a radial thrust bushing, counterbalanced and sealed by a packing gland. The two lower stirring arms are water-cooled, but the top leveler arm is not cooled. Horizontal rotation and vertical motion is controlled within limits by setting of the variable-speed drive and limit switches. The stirrer usually is rotated at one-half revolution per minute and the vertical movement is limited to 2 feet. In practice, the stirrer passes through the bed in 15 minutes, but this rate can be slower or faster, depending upon coal properties. The lowest point reached by the stirrer is usually set 2 feet above the top of the grate, but may reach within 1 foot of the grate.

Nuclear density gages are used to indicate conditions within the pressure vessel. Ash zone, bed level, and voids in the bed are detected with these gages (ref. 5).

Procedures

Startup is made by igniting kindling wood and charcoal covered with a layer of anthracite (pea size, 9/16 by 13/16 inch). The grate is protected from overheating during startup by a covering of ash upon which the fuel was placed. Anthracite was used during startup to avoid depositing tar in the cold system. Admission of steam was started and the air rate increased when combustion was established, as indicated by rising gas temperatures. More anthracite was added until full bed depth was reached. Combustible gas was produced within 1-2 hours from ignition. Coal feed was changed from anthracite to bituminous when off-take temperature reached 1,000° F. Approximately 4 hours were required for the anthracite to burn out and be completely replaced by a bituminous coal bed.

Air supply was set at a selected rate, and a constant inventory of fuel was maintained by adding coal in small increments of 250 to 300 pounds whenever a signal from a nuclear density gage indicated fuel was low. Steam admission was estimated initially based on the expected

---

*The authors are with the U.S. Energy Research and Development Administration, Morgantown Energy Research Center, Morgantown, West Virginia.

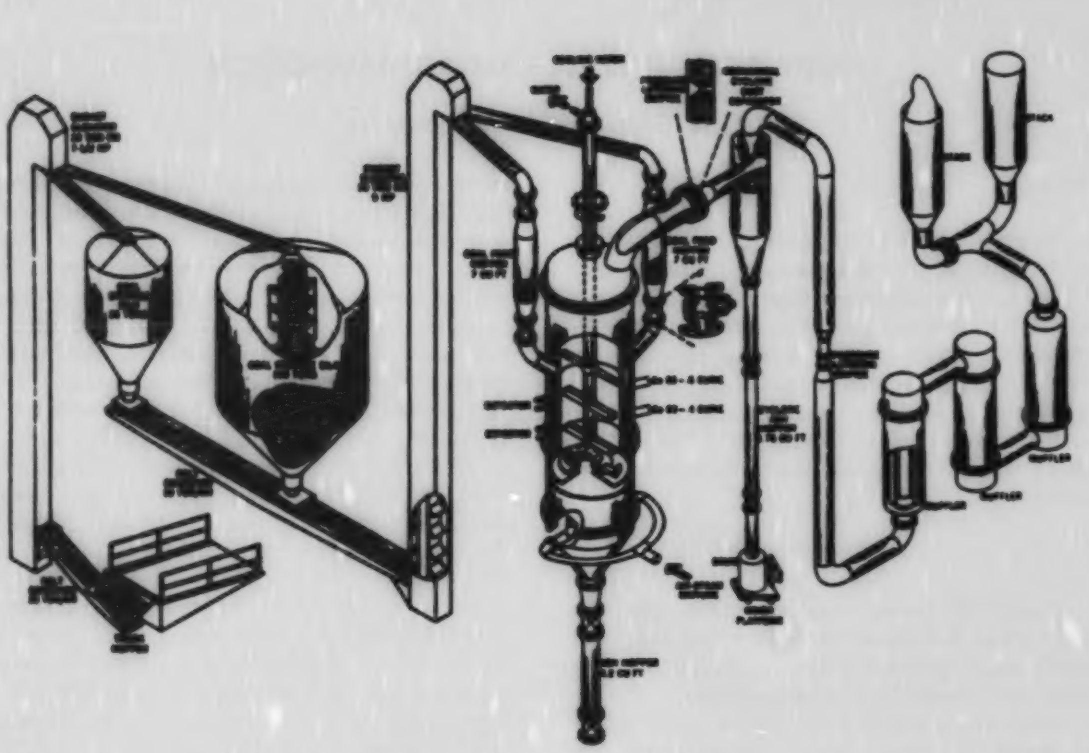


Figure 1. MERC stirred-bed gasification system.

coal rate and known burning characteristics of the fuel. Weight ratio of steam to coal was close to 0.5, but could be more or less for a particular coal as adjustments were made seeking optimum performance and steady operation.

A data period was started when steady conditions were attained as shown by a constant coal rate over several hours. Conditions were not changed during a data period. Should a change in conditions be necessary, the data period was terminated and a new period started when steady conditions were reached again. Samples collected during a data period included dust, tar, and water entrained in the gas, cyclone dust, and ash. Dust, tar, and water content of the product gas was calculated based upon the weights collected from a sample (about 25 scfh) of measured volume taken over a timed interval.

Operating data and analyses for a variety of coals are given in tables 1 and 2.

Gas Sampling and Analysis

The system in figure 2 was developed to remove and recover all particulate matter, tar and water from a measured sample stream and deliver a clean gas to several process analyzers.

The sample inlet tap is located in a muffler between the flares and the pressure let-down orifice. The inlet tap is located flush with the muffler wall with no provision for isokinetic sampling. The sample offtake pipe is maintained higher than 800° F. to prevent tar condensation in the high-temperature dust filter. Tar is removed in a 40 kV, steam-traced, electrostatic precipitator. Water and light oils are condensed with a small water-cooled heat exchanger. The gas stream is then vacuum pumped through a series of dry absorbents (silica gel and drierite) to protect the dry gas meter and pump and to deliver a clean gas to the process analyzers.

Table 1. Analyses of coals, bottom ash, and tars from producer runs

Coal Run-Period	New Mexico Sub-Bit. 62-2	Kentucky #9 64-1	WV Upper Freeport 61-5	Illinois #6 39-7	WV Arkwright 71-3	WV Loveridge 52-4	WV Middle Kittanning 45-3
A. Coal							
FSI	2	4-1/2	8-1/2	4-1/2	8	8	-
H_2O %	8.8	5.0	1.0	9.2	1.1	6.3	2.0
Ash	24.2	15.4	20.3	8.5	8.3	8.0	8.3
C	50.8	64.5	66.8	66.7	75.9	76.2	79.4
H	5.1	5.5	4.4	4.6	5.7	5.7	5.7
S	1.0	3.9	3.8	1.3	2.7	2.9	1.1
N	1.6	1.7	1.2	-	1.4	-	-
O*	8.5	4.0	3.5	-	4.9	-	-
Btu/lb	8900	11450	11580	12000	13675	13755	14000
B. Bottom Ash, %, (Dry Basis)							
Ash	94.6	96.2	92.3	84.3	89.7	77.6	82.5
C	4.1	1.2	6.0	12.9	8.4	20.2	15.9
H	.6	.3	1.5	1.2	.2	1.7	1.1
S	.2	2.1	.5	1.2	.3	.8	1.1
C. Tar,% (Dry Basis)							
Ash	8.1	11.6	0.0	-	0.0	.2	5.0
C	77.6	70.7	84.5	-	86.1	83.2	88.0
H	6.6	7.2	6.9	-	5.4	6.0	4.0
S	1.3	2.4	2.0	-	1.9	1.1	1.0
N	1.6	1.7	-	-	1.3	-	-
Btu/lb	13565	14000	16000	-	15735	15896	16000

* By difference

Table 2. Operating data and test results from producer runs

Coal	New Mexico Sub-Bit.	Kentucky #9	WV Upper Freeport	Illinois #6	WV Arkwright	WV Loveridge	WV Middle Kittanning
Run-Period	62-2	64-1	61-5	39-7	71-3	52-4	45-3
Pressure (psig)	145	207	119	17	134	90	45
Input, lb/hr							
Coal	1800	1987	1196	1030	1376	1330	866
Air	4583	5708	4033	2350	4994	4419	3084
Steam	763	987	501	322	635	641	400
Input Ratios, lb/lb							
Steam:Coal	.4	.5	.4	.3	.5	.5	.5
Air:Coal	2.6	2.9	.34	2.3	3.6	3.3	3.6
Output, lb/hr							
Ash	330	243	135	69	101	132	110
Cyclone Dust	86	18	16	28	6	20	10
Gas	5784	8096	5375	3322	6647	5705	3906
Tar	53	21	19	23	29*	52	41
Water	889	348	182	242	444	481	283
Gas Yield							
MSCFH	77.7	101.4	74.7	44.2	88.6	83.2	58.6
SCF/LB coal	43.4	54.4	64.7	47.0	65.4	61.1	64.2
Gas Analysis							
CO	15.3	18.1	22.5	21.8	19.1	19.8	23.9
CO_2	12.7	11.0	7.1	6.9	8.8	9.5	7.6
N_2	59.3	54.4	53.6	51.5	55.4	52.0	51.5
H_2	10.7	13.3	14.0	17.8	12.8	15.8	14.7
CH_4	2.1	2.0	2.5	2.0	2.9	2.9	2.2
C_2H_6	0.0	.2	0.0	.2	.3	0.0	.2
H_2S	.2	.9	.3	.2	.5	.2	.1
O_2	0.0	.1	0.0	-	.1	-	-
Heating Value Btu/CF	104	128	142	153	138	144	151

* Average for several periods.

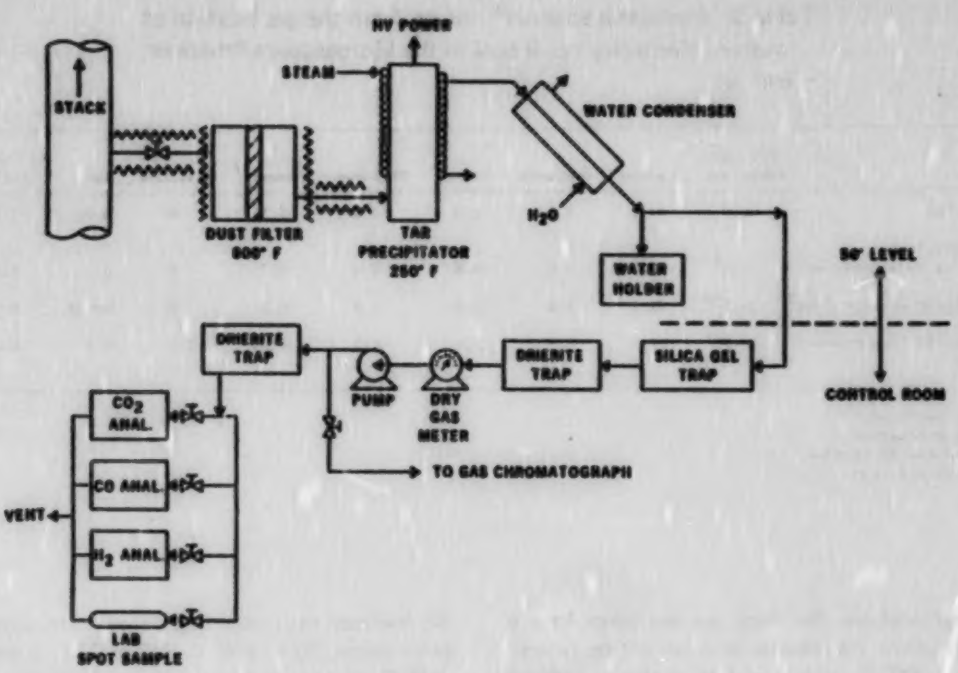


Figure 2. Gas sample system for pressurized gas producer

CO and CO_2 levels are monitored by infrared analyzers and H_2 by a thermo-conductivity analyzer; fluctuations in component concentrations will alert the operator to malfunctions such as stirrer breakdown, bed void formation and improper coal feeding. An oxygen analyzer has been added to detect O_2 levels above .1 percent. The presence of oxygen indicates a vacuum leak usually caused by a dust plug in the sample inlet.

The gas chromatograph is a dual column, thermal-conductivity type analyzer which records on a 7-minute cycle the major components, N_2, CO_2, CO, H_2, CH_4, C_2H_6, and H_2S.

Following a typical test period of 24 hours, the dust filter, tar trap, and condensed water plus absorbent traps are weighed; the dust and tar were analyzed for ultimate, proximate, and heating value analyses. Results of these analyses are used to obtain overall producer material and heat balances.

DISCUSSION

Direct measurement of gas production was impossible because metering devices rapidly clogged with tar and dust and became inoperative. Gas production was calculated by obtaining a preliminary value from a mass balance in which gas output was taken as the difference between the input (coal + air + steam) and the output (bottom ash, dust, tar, and water). This preliminary gas yield was used to calculate balances for carbon, hydrogen, nitrogen, oxygen, and sulfur. Values of the output/input ratio falling between 0.9 and 1.1 were taken as acceptable data for gas production. Carbon and nitrogen balances generally gave ratios falling within the desired range, hydrogen and oxygen balances were less frequently suitable, and sulfur balances seldom produced suitable ratios. Gas productions given in the report met the output-input test.

Operating runs for seven coals, given in tables 1 and 2, were selected further to be typical of the respective fuels based on carbon in the bottom ash, heating value of the product gas and length of the run. These values are averages for the period and do not necessarily represent the optimum for any particular coal. It is recognized that changes have occurred in operating mode and data collection over the years during which the producer was operated.

Table 3. Elemental analysis[1] of tar from the gasification of Western Kentucky no. 9 coal in the Morgantown Producer (ref. 6)

	Pct. of total tar	Carbon	Hydrogen	Sulfur	Nitrogen	Oxygen[2]	Moisture	Ash	H:C atomic ratio
Whole tar	100.0	82.1	7.6	1.0	1.0	8.3	0	0.07	1.11
Tar fractions									
Soluble in n-pentane[3]	31.4[4]	82.3	7.8	0.8	0.4	8.7	0	0	1.13
Insoluble in n-pentane[3]	50.6[4]	82.2	6.6	1.6	1.5	8.1	0	trace	0.96
Insoluble in benzene	18.0[4]	71.0	4.9	1.9	1.5	7.0	2.2	11.5	0.83

1/ As received.
2/ By difference.
3/ Soluble in benzene.
4/ Moisture free.

For tar analyses, the dirty gas was taken from a sidestream before the pressure let-down orifice, filtered at 800° - 1,000° F. to remove dust, cooled to ambient air temperatures, and a tar-water emulsion was collected in a series of water-cooled traps. The emulsion was broken and water was separated by distillation.

Table 3 summarizes data on whole tar as collected by the University of Kentucky from producer tests in Morgantown, West Virginia, in 1972 (ref. 6). By infrared analysis of the asphaltene fraction (benzene-soluble, pentane insoluble) and ultraviolet spectra of a cyclohexane extract of asphaltenes, 54 compounds were identified including basic structures such as phenols, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, picene, pentacene, dibenzofluorene, and dibenzopyrene. Infrared analysis of the residue fraction was weakened by the presence of ash, but revealed highly aromatic structures as well as phenolic oxygen compounds.

In 1973, a tar sample was taken from a producer run with Navajo, New Mexico, subbituminous coal. Light oil and water were distilled from the tar which was extracted by a series of solvents. Cyclohexane extraction gave 39.7 percent soluble (oils) and 60.3 percent insoluble; the cyclohexane insoluble when extracted with benzene showed 22.8 percent benzene-soluble (asphaltenes) and 37.5 benzene-insoluble on an original tar basis. Successive extraction of the cyclohexane-soluble portion revealed only a trace of tar acids and no tar bases.

Recently a tar sample was collected from a producer run with Pittsburgh-seam coal. The tar was stripped of water and fractionally distilled at 20 mm Hg. The light oil fractions were combined to represent three boiling point ranges, 20 to 240° C, 240 to 320° C, and 320 to 340° C and analyzed by gas chromatography; the pitch, representing 69 percent of the tar, is being analyzed.

Table 4 gives the analyses of the respective fractions and shows again the wide assortment of chemical species in the light portion of the tar.

Finally, grab samples of the raw producer gas from a run with Pittsburgh-seam coal showed COS ranging from 315-350 ppm, NH_3 from 529-1,028 ppm and HCN less than 10 ppm with H_2S analyses of 4,500-4,800 ppm.

Table 5 gives analyses of bottom ash from two coals, showing the excellent agreement between x-ray and wet chemical results.

SUMMARY

Although considerable data have been amassed on producer runs with a variety of coals over a range of operating conditions, providing yields and analyses suitable for calculating material and heat balances, little information has been published on the analyses of tar and trace constituents in the gases.

This report presents some tar analyses for runs with three different coals and indicates the quantity of COS and NH_3 in a producer gas from Pittsburgh-seam coal.

Elaborate plans are laid to obtain detailed analyses on solids, water, tar, and gas from producer runs with three different coals. This will include isokinetic sampling and dust particle size distribution.

Table 4. Analysis of light oil fraction of producer tar from Pittsburgh-Seam coal

Distillate Fraction, °C	20 - 240	240 - 320	320 - 340
% of Tar	11	17	3
Consitituents in light oil,%			
Phenol	4.88	0.48	-
O-Cresol	4.18	0.68	-
M-P-Cresol	10.68	0.14	-
Indan	4.77	0.47	-
Indene	1.89	-	-
Xylenols	18.64	3.36	-
Naphthalene	20.63	4.30	-
2-Methylnaphthalene	9.28	6.29	-
1-Methylnaphthalene	4.66	5.23	-
Dimethylnaphthalenes	1.63	18.06	1.32
Ethylnaphthalene	1.23	5.19	-
Acenaphthene	-	8.88	1.89
Dibenzofuran	-	6.38	1.97
Fluorene	-	5.71	7.34
4-Methyldibenzofuran	-	4.57	7.09
3-& 2-Methyldibenzofuran	-	1.93	7.73
Methylflorenes	-	2.84	23.90
Phenanthrene	-	0.44	15.94
Methylanthrene	-	-	8.81
Fluoranthenes	-	-	0.28
Unknowns	17.53	25.05	23.73

PLANS

It is recognized that gasification of high-sulfur coals with air and steam is meaningless unless economic methods are developed to remove H_2S and other constituents prior to combustion of the low-Btu fuel gas in boilers, furnaces, or turbines.

MERC is operating a 16-inch diameter atmospheric producer (10,000 scfh) to study removal of H_2S from hot gas by means of an iron oxide absorber system.

Also, a wet system is being installed, for operating early in 1976, on a sidestream of the gasifier (30,000 scfh) to water scrub the raw producer gas and to study combustion of the cleaned gas in a turbine simulator.

In both programs all gaseous, liquid, and solid products will be analyzed extensively for major, minor, and trace constitutents.

ACKNOWLEDGMENTS

The authors express their thanks to Paul S. Lewis, Robert V. Rahfuse, and Scott Marshall for their assistance in assembling the data on producer runs and analyses. Special recognition is given to J. R. Comberiati for performing the tar analyses.

Table 5. Analysis of bottom ash from producer runs

Coal	Pittsburgh Seam		Western Kentucky No. 9 (ref. 7)
Anal. Method	Wet	X-ray	Wet
Constituent, %			
SiO_2	44.9	45.0	45.9
Al_2O_3	27.3	23.3	18.2
Fe_2O_3	17.0	17.1	23.2
CaO	4.8	5.1	6.2
MgO	1.3	2.2	0.9
Na_2O	1.0	1.6	0.5
K_2O	1.5	1.3	2.2
P_2O_5	.3	.2	0.2
TiO_2	1.3	1.3	1.0
SO_3	-	-	1.6
Total	99.4	97.1	99.9

REFERENCES

1. R. V. Rahfuse, A. J. Liberatore, and G. R. Friggens, "Gasification of Caking-Type Bituminous Coal at 75 to 150 psig in a Stirred-Bed Producer," U.S. ERDA, MERC/TPR-75/3, July 1975, 11 pp.
2. P. S. Lewis, A. J. Liberatore, R. V. Rahfuse, and G. R. Friggens, "Bituminous Coal Gasified in a Stirred-Bed Producer," U.S. ERDA, MERC/RI-75/1, June 1975, 16 pp.
3. R. V. Rahfuse, G. B. Goff, and A. J. Liberatore, "Noncaking Coal Gasified in a Stirred-Bed Producer," BuMines TRP 77, March 1974, 8 pp.
4. P. S. Lewis, A. J. Liberatore, and J. P. McGee, "Strongly Caking Coal Gasified in a Stirred-Bed Producer," BuMines RI 7644, 1972, 11 pp.
5. G. R. Friggens and A. W. Hall, "Nuclear Gages for Monitoring the Coalbed of Commercial-Scale Pressurized Gas Producer," BuMines RI 7793, 1973, 9 pp.
6. *Third Quarterly Progress Report: A Kentucky Coal Utilization Research Program*, Institute for Mining and Minerals Research, University of Kentucky, April 30, 1973, pp. 23-27.
7. *Seventh Quarterly Progress Report: A Kentucky Coal Utilization Research Program*, Institute for Mining and Minerals Research, University of Kentucky, May 1974, pp. 15-19.

THE WESTINGHOUSE FLUIDIZED BED COMBINED CYCLE PROCESS: STATUS OF TECHNOLOGY AND ENVIRONMENTAL CONSIDERATIONS

L. A. Salvador, E. J. Vidt, and J. D. Holmgren*

Abstract

The conversion of coal to a clean, low Btu gas which can fuel a combined-cycle power generation plant holds promise of being one of the most economic, efficient, and environmentally acceptable methods of utilizing our coal resources to provide the nation's energy needs. Westinghouse Electric Corporation as leader of a six-member government/industry team is developing this power generation system utilizing a multiple-fluidized bed process for devolatilization, desulfurization and gasification of coal to produce low-Btu fuel for a combined-cycle power generation package.

The Westinghouse team is implementing one of the first totally integrated coal conversion programs, from bench-scale to a complete coal to electric power energy conversion package. Begun in 1972, the program is presently in the design and development phase. Bench-scale development activities are being performed in conjunction with the operation of a 1200 pounds per hour process development unit (PDU) to evaluate process feasibility and operability. In addition, a conceptual design for full-scale generating plant has been completed.

The lab and pilot scale testing has been directed toward a number of technical and environmental considerations including the behavior of high-sulfur, caking coals, ash removal and disposal, sulfur removal and disposal, control of combustion product effluents, turbine protection, and product gas cleaning. The recent encouraging results of these studies indicate that operation of the system to provide power in an efficient and environmentally acceptable way is feasible.

INTRODUCTION

Putting aside all of the rhetoric of recent years relative to the existance or nonexistence of an energy crisis, three facts remain clear:

(1) Energy needs will continue to grow as population increases.

(2) The use of natural gas and petroleum, because of diminishing supplies, will someday decline relative to coal, nuclear, and other energy sources in supplying our energy needs.

(3) We must find ways to economically utilize our coal resources compatible with our desire for a clean, high quality environment.

The work described in this paper grew out of a realization that the above factors would be important considerations, particularly in the electrical utility industry, and also that a new type of power plant was needed which could meet the new restrictions on sulfur oxides, nitrogen oxides, particulates, and other emissions; which could burn domestic high-sulfur, caking coals; which could generate power more economically than present generating plants at intermediate capacity factors of 30-50 percent; and which could make the most efficient use of our coal resources. The system concept chosen to fulfill these criteria is an advanced, multiple fluidized bed coal gasifier which produces a clean, low-Btu fuel gas to be burned in a pre-engineered, packaged, combined cycle generating plant composed of both steam and gas turbines and a waste heat recovery system.

The present goal of the program is the integration and operation of a gasifier/power-generating plant on the Public Service of Indiana system at the Dresser Station in Terre Haute, Indiana. To achieve this goal, a government/industry team was assembled. The team is composed of members with broad interests which functionally integrate the project: Amax Coal and Peabody Coal, coal raw material producers; Bechtel Incorporated, an architect-engineer and plant constructor; Public Service of Indiana, a public utility; Westinghouse Electric, a producer of electrical generating and transmission equipment; and the Energy Research and Development Administration, the sponsoring government agency. Figure 1 illustrates the team membership and functional responsibilities and relationships. Other associate members sponsoring the program include Northern Indiana Public Service, Tennessee Valley Authority, Consumers Power, Union Electric, Duke Power, New England Electric System, Columbus and Southern Ohio Electric, Pennsylvania Power and Light, Montana Power, Iowa Power and Light, and Tampa Electric.

The Westinghouse program is totally integrated. Tasks and goals are laid out to include a step-by-step approach from bench-scale laboratory research, pilot scale development and system design and evaluation to the operation of the demonstration plant. The latter is of sufficient capacity to represent a viable commercial plant. Figure 2 illustrates the task orientation on a time scale indicating the anticipated full-scale plant operation in the 1980-1983 time period.

---

*The authors are with Westinghouse Research Laboratories, Pittsburgh, Pennsylvania.

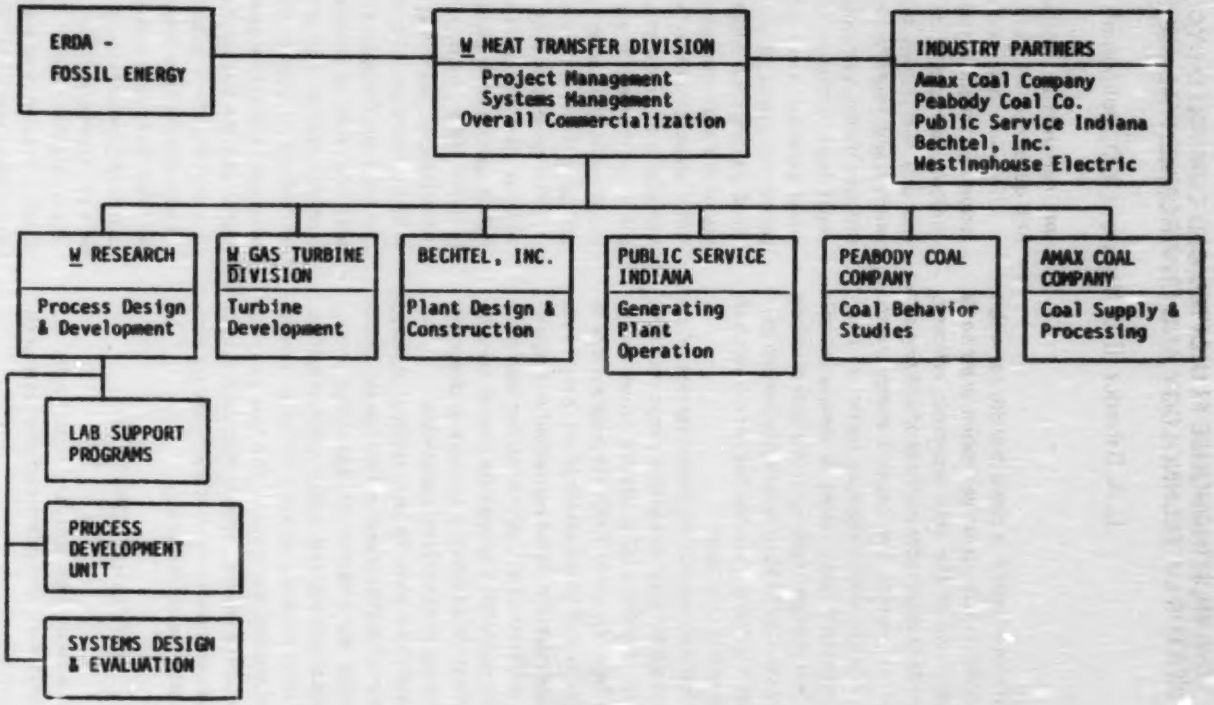

ERDA - FOSSIL ENERGY
W HEAT TRANSFER DIVISION
Project Management
Systems Management
Overall Commercialization
INDUSTRY PARTNERS
Amax Coal Company
Peabody Coal Co.
Public Service Indiana
Bechtel, Inc.
Westinghouse Electric
W RESEARCH
Process Design & Development
W GAS TURBINE DIVISION
Turbine Development
BECHTEL, INC.
Plant Design & Construction
PUBLIC SERVICE INDIANA
Generating Plant Operation
PEABODY COAL COMPANY
Coal Behavior Studies
AMAX COAL COMPANY
Coal Supply & Processing
LAB SUPPORT PROGRAMS
PROCESS DEVELOPMENT UNIT
SYSTEMS DESIGN & EVALUATION

Figure 1. Westinghouse program organization.

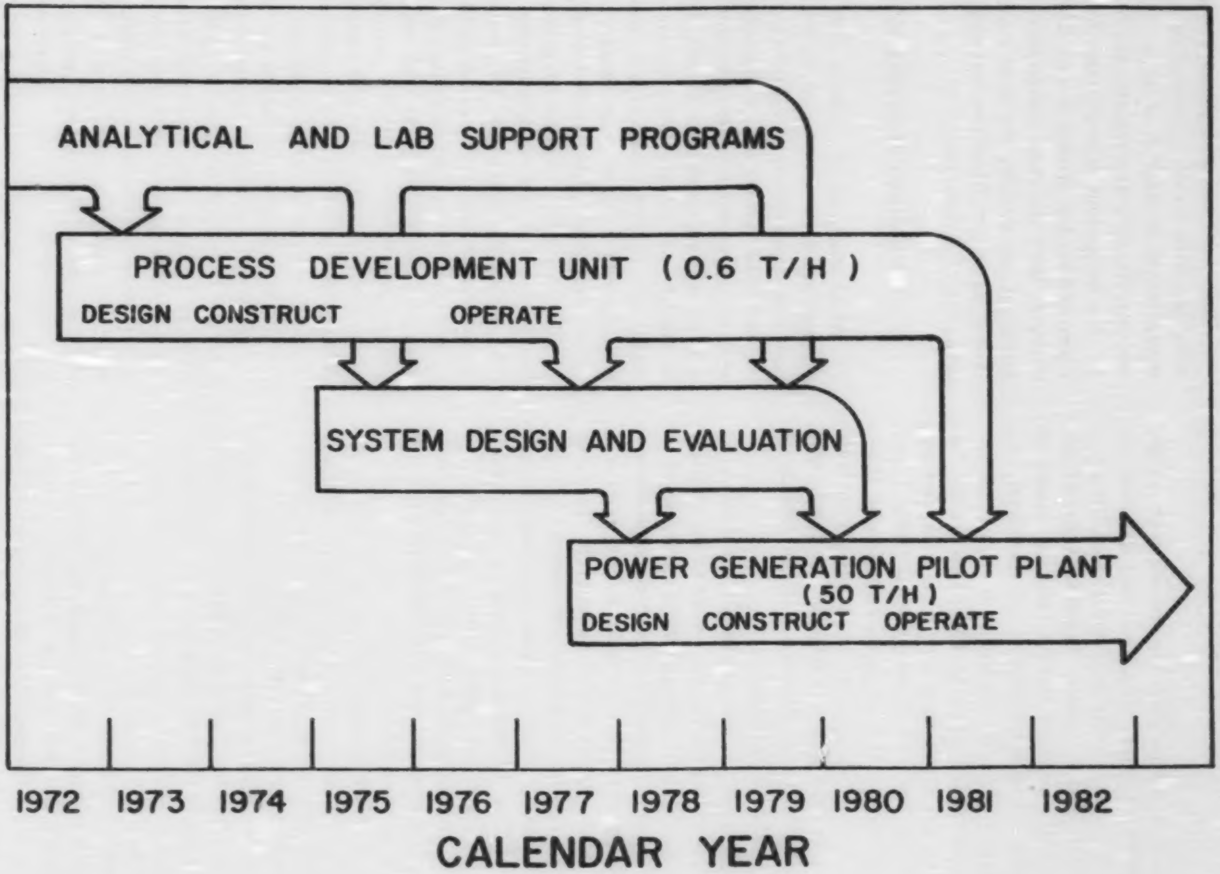

ANALYTICAL AND LAB SUPPORT PROGRAMS
PROCESS DEVELOPMENT UNIT (0.6 T/H)
DESIGN CONSTRUCT OPERATE
SYSTEM DESIGN AND EVALUATION
POWER GENERATION PILOT PLANT (50 T/H)
DESIGN CONSTRUCT OPERATE
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
CALENDAR YEAR

Figure 2. Program tasks and goals.

THE PROCESS

Figure 3 is a simplified diagram which shows the main features of the process. Coal and dolomite are crushed, sized, and dried prior to being fed to the gasification system. Hot fuel gases composed largely of carbon monoxide, hydrogen, and nitrogen are cleaned of particulates and combusted with air in a combustor. The hot combustion gases are expanded through a gas turbine which produces about 95 MW of electricity. Exhaust gases from the turbine are then used to generate steam in a heat recovery steam generator (HRSG), and the steam is expanded through a steam turbine which produces another 40 MW of electricity. Two such gasifier modules can also be employed with two 95 MW Westinghouse 501D gas turbines and one 80 MW steam turbine to produce 270 MW.

With the exception of the low-Btu gas combustor, the power generating equipment is more or less standard equipment of the kind currently fired by natural gas or fuel oil. The gasifier reactors, on the other hand, are new concepts currently under development. Figure 4 is a closer look at the details of these subsystems. The fresh coal is pneumatically transported and injected into the devolatilizer reactor where it mixes with 1600° F char and passes at 20 to 40 feet per second up a "draft tube" on the center line of the reactor. The high velocity and dilution with char prevent particles of caking coals from agglomerating as they become plastic on the surface and give up their volatile matter.

As the gases are evolved from the coal in the reactor, they pass through a shower of dolomite particles which remove the sulfur present as hydrogen sulfide. These sulfided dolomite particles, heavier than the char formed from the devolatilization of coal, migrate to the bottom of the fluidized bed along with some char which recirculates around the draft tube in the "downcomer."

Char and dolomite are discharged separately through ports at different elevations in the reactor. Spent dolomite is collected for oxidation to the sulfate and disposal or alternatively for regeneration and recycle to the devolatilizer. Char is fed to the gasifier reactor where it is totally consumed by combustion with air and by reaction with steam at temperatures from 1900° F to 2100° F. These reactions provide a hot fluidizing gas composed of carbon monoxide, nitrogen, and hydrogen to provide heat to the devolatilizer which is mildly endothermic.

In the process of combusting the char at 2100° F, the ash reaches its softening point and begins to agglomerate. Larger, heavier ash particles become defluidized, fall from the bed, and are continuously drawn off at the bottom of the reactor.

Gases from the devolatilizer contain some particulates, but little tar or oils which are cracked to lighter hydrocarbons at 1600° F or above. The particulates are removed via cyclones and a sand bed filter.

For the generating plant with "once through" utilization of dolomite, an overall material balance is given in figure 5. With dolomite regeneration and recycle, the quantities are basically the same except that dolomite feed is reduced to 3 tons per hour and waste dolomite is reduced to 2 tons per hour.

CURRENT PROGRAM STATUS

While many of the portions of the Westinghouse process have been tested by others, the feasibility of this particular combination of subsystems has not yet been demonstrated. To do this, a well-balanced program of analysis, lab bench-scale research, and pilot scale development is being conducted. As one can see from figure 6, the lab-scale research projects cover the important areas of coal fluidization and processing, systems analysis, sulfur removal, gas cleaning, combustion and turbine expansion. These will be discussed later.

The pilot development is being conducted in a 1200 pounds per hour process development unit (PDU). The PDU was built in 1973 and 1974, and mechanical completion was achieved in September 1974. Figures 7 and 8 are two views of the plant and figure 9 shows the control room from which essentially all operations and data acquisition in the plant are controlled. Following mechanical completion, the plant was commissioned in January 1975 and all of the process and auxiliary subsystems were run at design conditions with the exception of the main reactors. During this period, a number of design and operational problems were encountered and solved. Typical of these problems—all of the ball valves in the plant were removed and repaired to prevent leaks; cyclone dip legs and fines pneumatic transport systems were redesigned to affect adequate fine removal; and cooling water systems were modified to operate with fines loadings heavier than were expected. In addition, two partial oxidation burners which utilize propane-air combustion with steam and carbon dioxide to produce a working gas for the devolatilizer were significantly redesigned, rebuilt, and successfully put online. Figure 10 summarizes these early tests and accomplishments with the PDU.

These efforts resulted in the first successful runs with coal in October 1975. The devolatilizer reactor was started up with Husky lignite char. Subbituminous coal was then fed to the reactor for 16 hours and devolatilized. The gas produced consisted of carbon monoxide, hydrogen, methane, carbon dioxide, water, and nitrogen

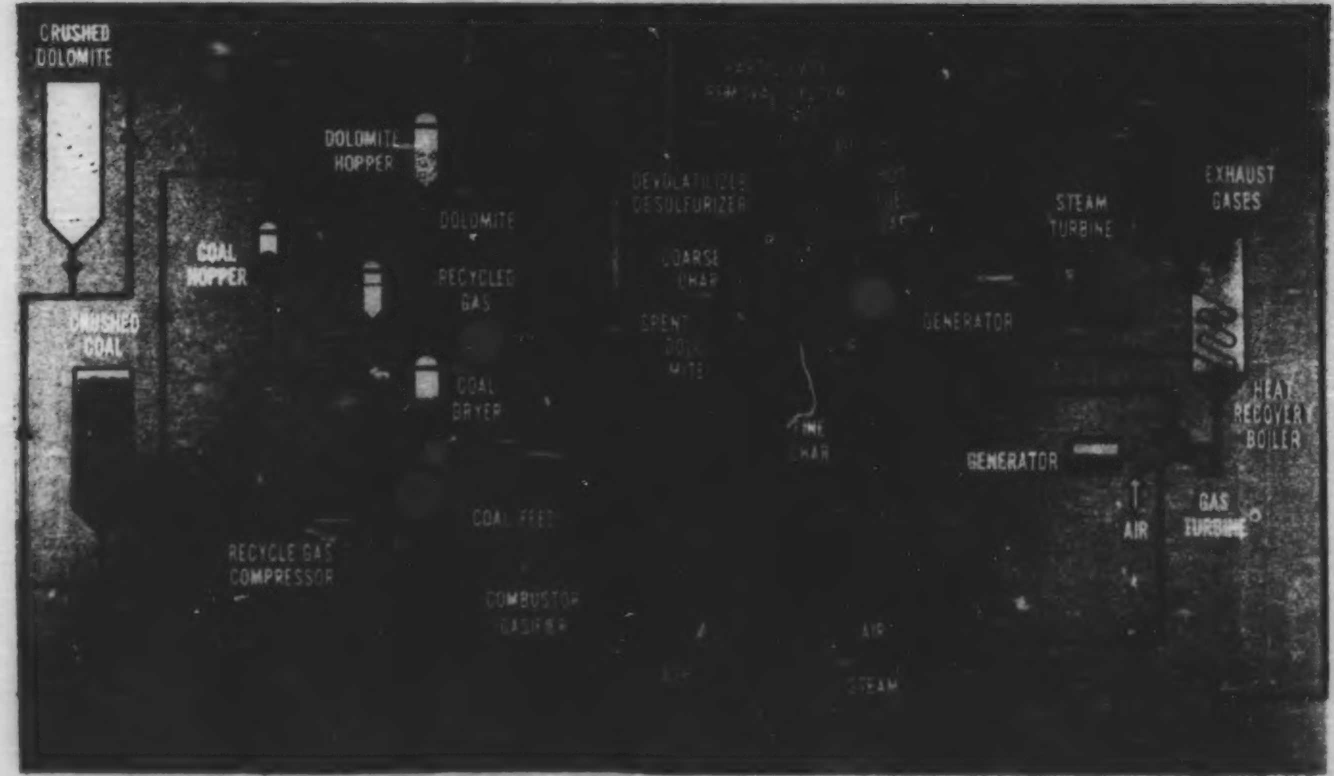

CRUSHED DOLOMITE
DOLOMITE HOPPER
COAL HOPPER
CRUSHED COAL
DOLOMITE
RECYCLED GAS
COAL DRYER
RECYCLE GAS COMPRESSOR
COAL FEED
COMBUSTOR GASIFIER
DEVOLATILIZER DESULFURIZER
COARSE CHAR
SPENT DOLOMITE
FINE CHAR
AIR
STEAM
GENERATOR
STEAM TURBINE
GENERATOR
AIR
GAS TURBINE
EXHAUST GASES
HEAT RECOVERY BOILER

Figure 3. Generating pilot plant.

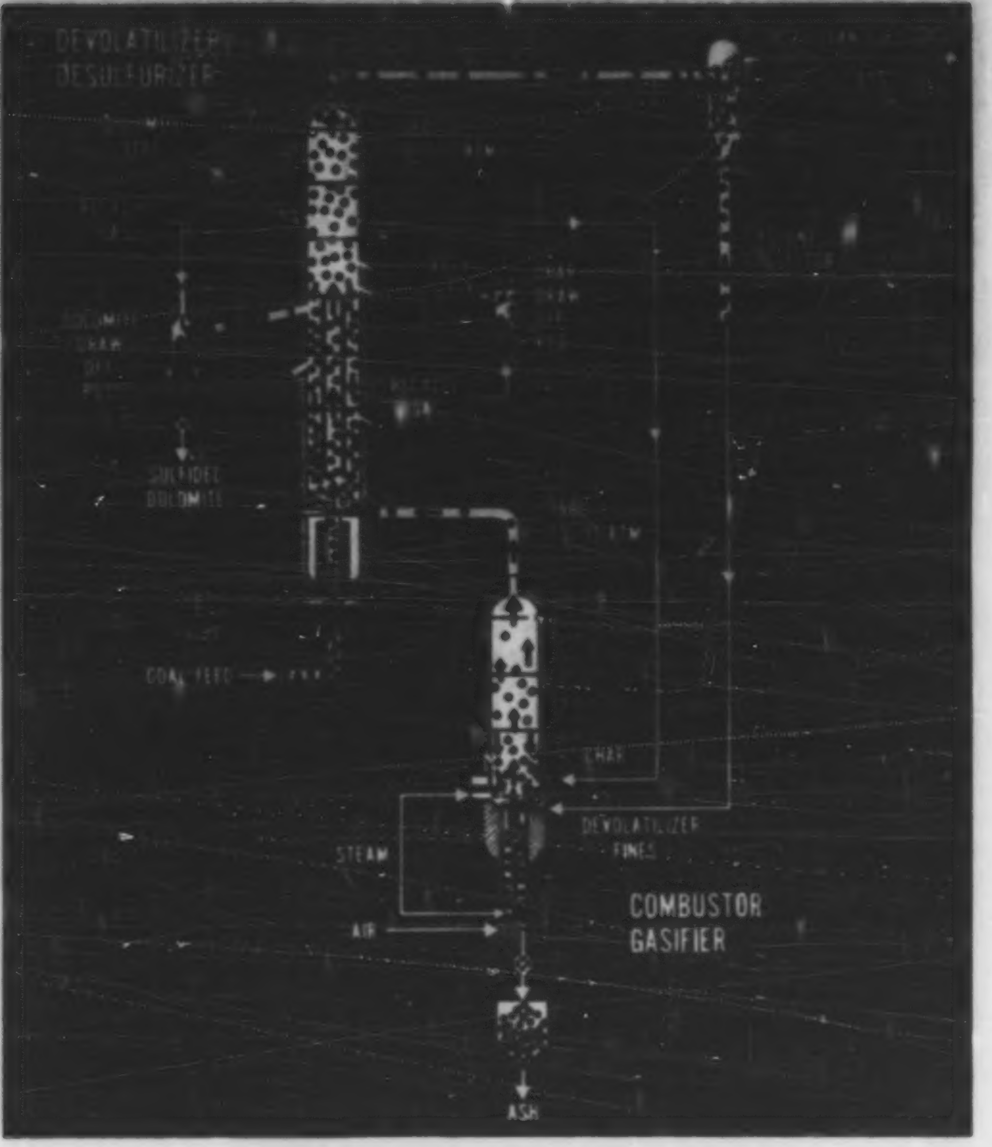

DEVOLATILIZER
DESULFURIZER
DOLOMITE
DRAW
OFF
SULFIDED
DOLOMITE
COAL FEED
CHAR
DEVOLATILIZER
FINES
STEAM
AIR
COMBUSTOR
GASIFIER
ASH

Figure 4. Westinghouse fluidized bed gasification process.

and had a heating value of 75 to 135 Btu/SCF. The exact composition and heating value is not being reported here because of some uncertainties in gas analyzer outputs which are currently being resolved.

As shown in figure 10, several important process and operational features were demonstrated during these initial tests with coal. Coal was continuously fed to the reactor, fluidized, devolatilized, recirculated around the draft tube, and discharged through the char removal systems. Slight particle growth by agglomeration was noted, and the char particles which formed appear to have high attrition resistance. Figure 11 shows cross sec-

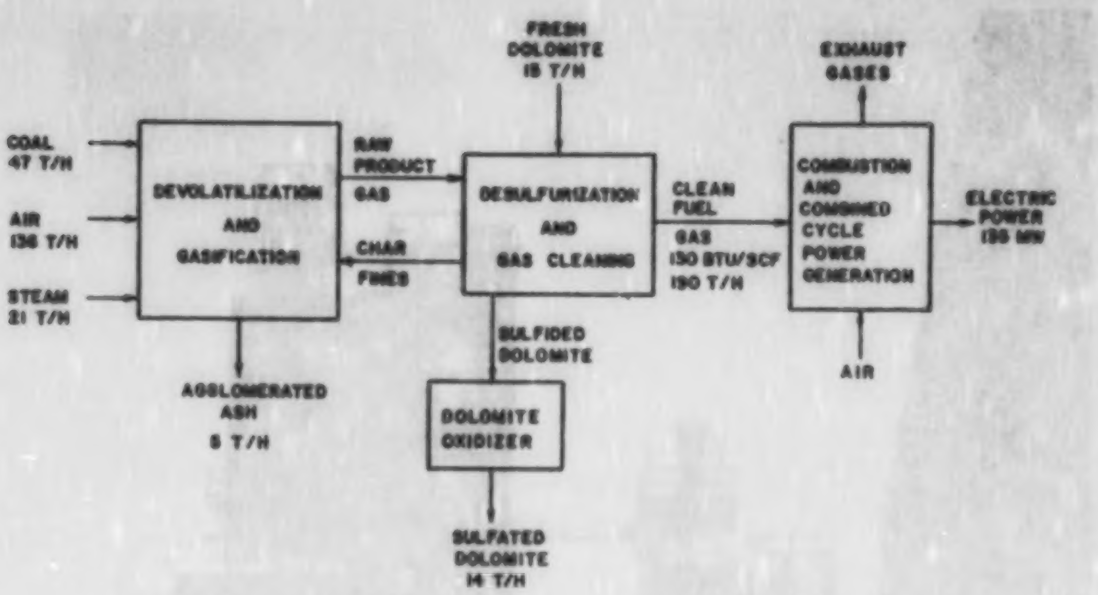

FRESH
DOLOMITE
15 T/H
EXHAUST
GASES
COAL
47 T/H
AIR
136 T/H
STEAM
21 T/H
DEVOLATILIZATION
AND
GASIFICATION
RAW
PRODUCT
GAS
CHAR
FINES
DESULFURIZATION
AND
GAS CLEANING
CLEAN
FUEL
GAS
150 BTU/SCF
190 T/H
COMBUSTION
AND
COMBINED
CYCLE
POWER
GENERATION
ELECTRIC
POWER
136 MW
AIR
SULFIDED
DOLOMITE
AGGLOMERATED
ASH
5 T/H
DOLOMITE
OXIDIZER
SULFATED
DOLOMITE
14 T/H

Figure 5. Simplified material balance 50 T/H generating plant with once-through dolomite utilization.

- Coal Processing
    - Fluidization
    - Coal Behavior
    - Sorbent Behavior
    - Reactor Analysis
    - Systems Analysis
- Gas Cleaning
    - Particulate Removal - Hot
    - Low Temperature Scrubbing
    - Hot Gas Cooling
    - Alkali and Trace Chemical Removal
- Combustion
    - Low Btu Gas Characterization
    - Combustor Development
    - Emissions Control
- Turbine Expansion
    - Tolerance to Chemical Species
    - Particulate Deposition
    - Erosion Tolerance

Figure 6. Analytical and lab support programs.

tions of the char particles produced showing the tendency for "popcorning" as volatiles are released. Figures 12 and 13 summarize the test conditions and results.

The PDU will continue to be used to evaluate process feasibility. In January, tests with dolomite injection with high-sulfur caking coals will begin. These will be followed by demonstrations of the adequacy of the gasifier and, later, the integrated operation of both reactors.

TECHNICAL/ENVIRONMENTAL CONSIDERATIONS

During this period of PDU testing, other activities are being directed toward the definition and solution of technical and environmental problems associated with the process. Leading this effort is the conceptual design of a 50 tons per hour plant which has recently been completed. This is being augmented by the lab and analytical studies mentioned above. Because the Westinghouse process was designed to solve environmental problems, the technical problems and environmental considerations are closely interrelated. In fact, the criteria for fuel cleanliness for the gas turbine may exceed the environmental criteria. Whereas these studies are by no means conclusive or complete at this time, the following brief discussion summarizes the present status of the process studies relative to several critical concerns.

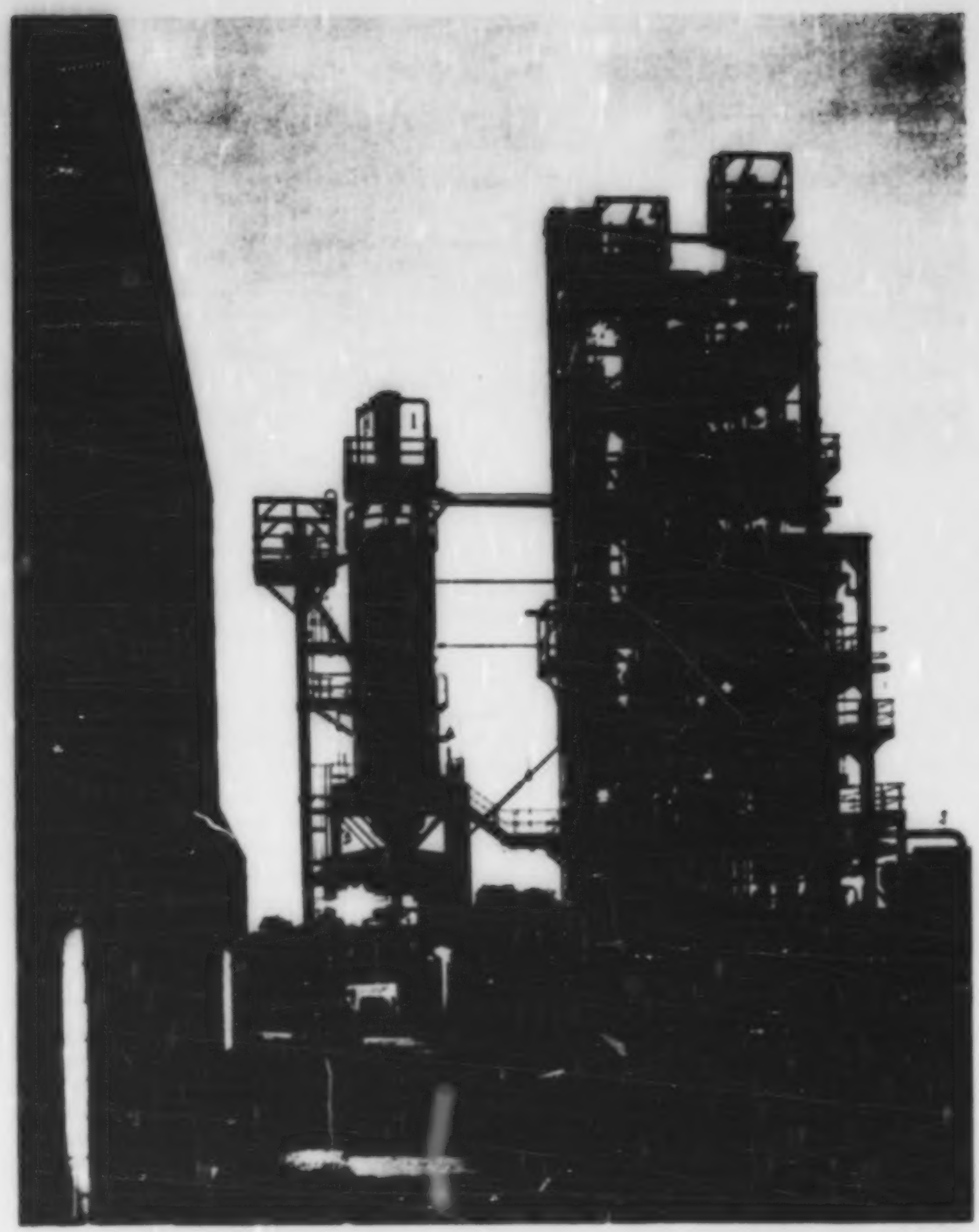


Figure 7. PDU process structure & operating building.

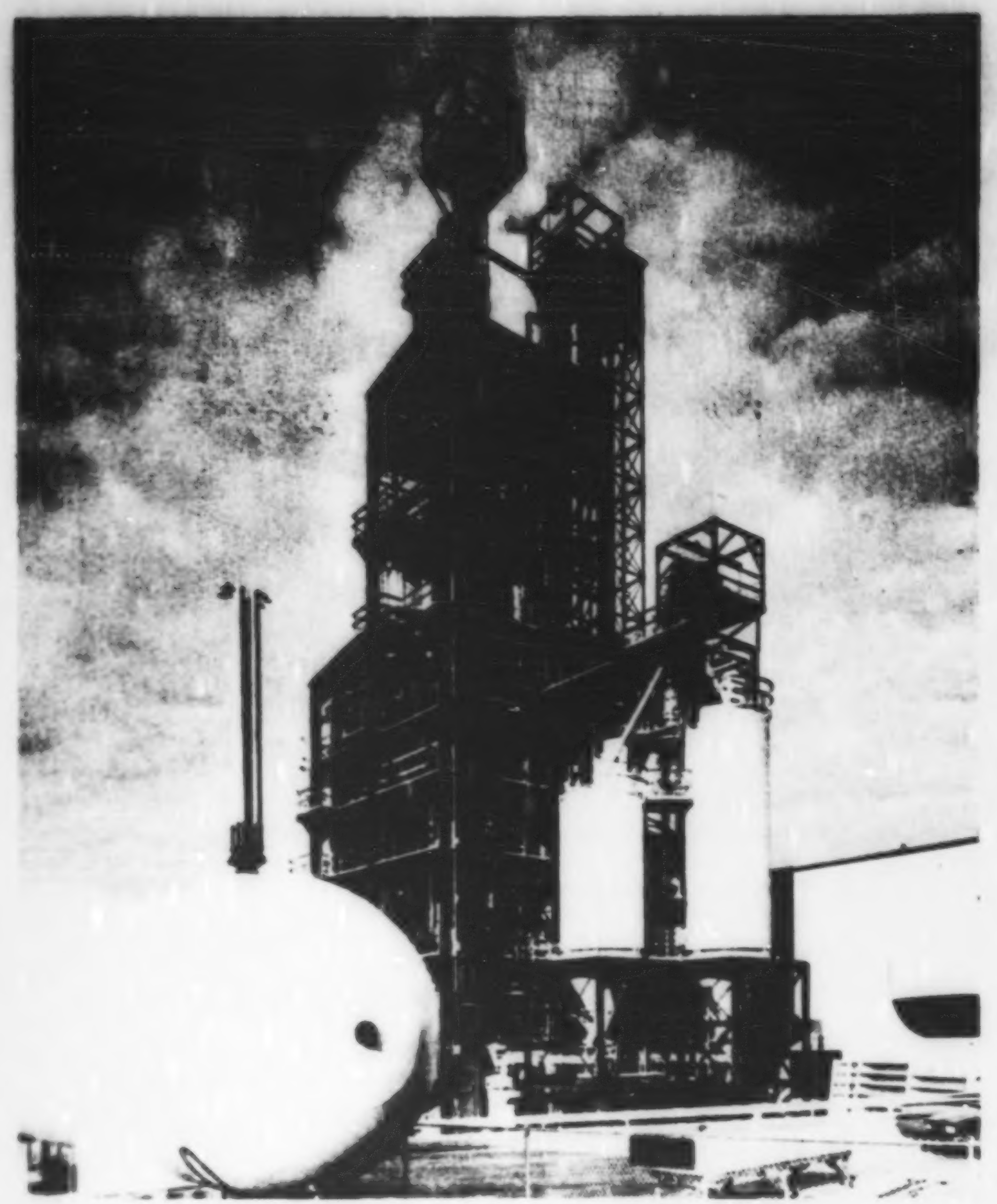


Figure 8. PDU process structure & raw materials storage.

Figure 9. PDU control room.

- Plant construction complete September 1974.
- All utility and auxiliary systems operated at design capacities and plant commissioned January 1975.
- Cold-flow solids feed and discharge and reactor fluidization studies with char completed May 1975.
- Synthesis gas generators testing completed September 1975. System redesigned, rebuilt, and tested at design conditions.
- Initial test of devolatilizer system with subbituminous coal successfully completed. Reactor fluidized at 1600° F subbituminous coal devolatilized, bed recirculation established, cyclone and char removal systems, cooling system, recycle gas system, tar-water waste disposal and thermal oxidation system operated continuously during 30-hour run October 1975.

Figure 10. Process development unit accomplishments.

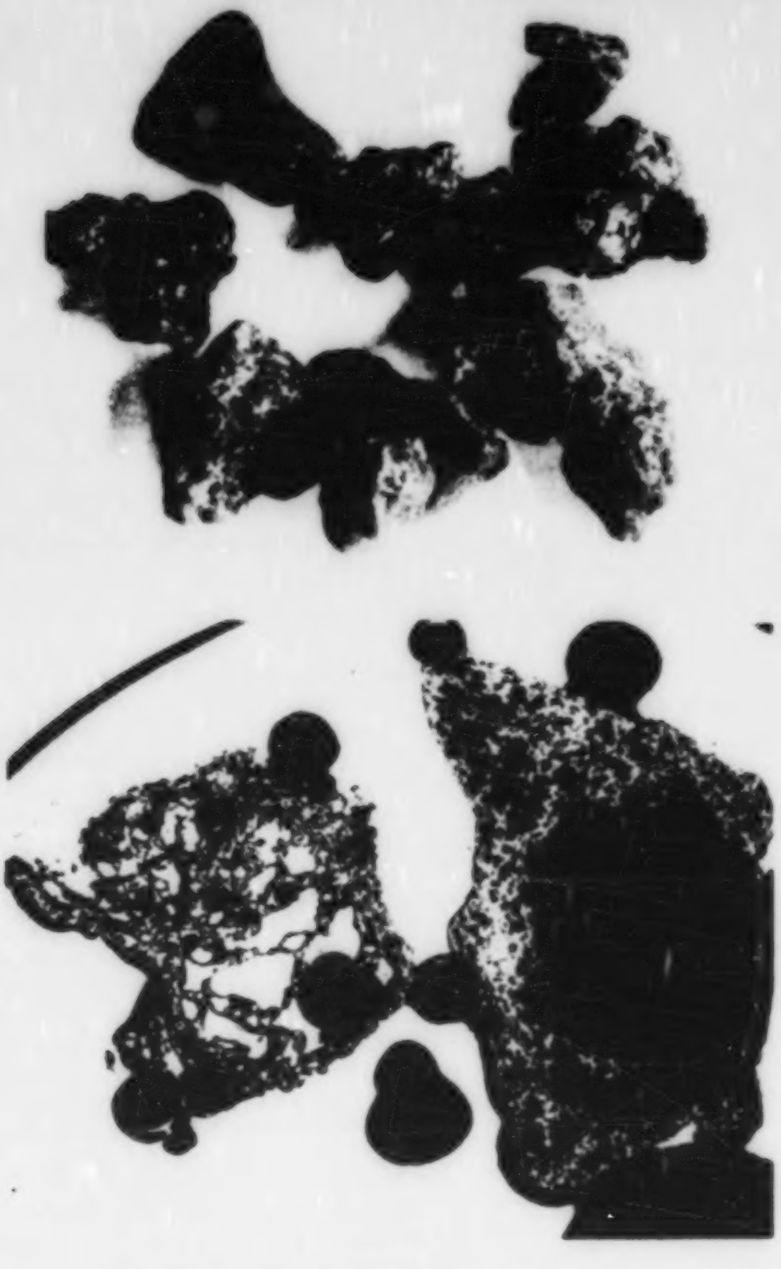


Figure 11. Devolatilized subbituminous coal.

Transport Gas Flow Rate	400 lb/hr
Inlet Flow Rate to Draft Tube	1200 lb/hr
Inlet Flow Rate to Downcomer	1200 lb/hr
Draft Tube Velocity	12-16 ft/sec
Downcomer Velocity	0.4-0.8 ft/sec
Freeboard Velocity	1.5 ft/sec
Transport Gas Temperature	200° F
Inlet Gas Temperature	2400° F
Reactor Bed Temperature	1600° F
Reactor Exit Temperature	1400° F
Coal Feed Rate	350 lb/hr
Char Withdrawal Rate	70-150 lb/hr
Fines Removal Rate	70-100 lb/hr
Bed Height	22 ft
Total Run Time at T ≅ 1600°	32 hr
Total Sub-C Coal Run Time	14 hr
Total Husky Char Run Time	18 hr

Figure 12. Summary of test conditions and results.

Sulfur Removal

The prime design for sulfur removal involves the use of dolomite at 1600° F in the devolatilizer reactor or, perhaps, in a second desulfurizer reactor where H_2S is adsorbed and reacted with the half-calcined stone. Two alternate schemes being studied are a lower temperature (1200° F) removal on a fixed bed of iron oxide and "cold," wet-scrubbing systems. Efforts on the prime system have centered around defining which selection criteria are important for dolomites and how well a number of dolomites available for use in the Terre Haute area conform to these criteria. Selection criteria include:

(1) Sulfur removal efficiency.
(2) Attrition resistance of the stone.
(3) Alkali metal release.
(4) Regeneration characteristics.
(5) Economic availability.

Figure 14 shows the economically available local dolomites in and around Indiana. These have been shown to have adequate sulfur removal characteristics. With feed rates based on a 1.2-to-1 calcium-to-sulfur ratio in the reactor and with a reactor volume to give a 1-second residence time, 90 percent sulfur removal is feasible. Fluidized bed studies show many stones to have excellent attrition resistance, notably Geneva, Salomonie, and Bonne Terre stones from Indiana and Canaan stone from Connecticut. Alkali release of potassium and sodium which causes turbine blade erosion and corrosion is smallest for Canaan, Geneva, and Salomonie stones. Regeneration of these stones has been adequately demonstrated in the laboratory, and it appears that 30 cycles of sulfidation and regeneration may be optimum.

In summary, sulfur removal and other stone criteria required for the generating plant can be met by locally available stones if the larger scale PDU tests corroborate lab studies. Stone disposal and regeneration processes continue to be a major effort of the program since in the final analysis, it will be a combination of economic and environmental values which prescribe the selection of "once-through" versus "dolomite recycle" plant designs.

	Inputs lb/hr	Outputs lb/hr
Coal	340	–
Downcomer Gas	1500	–
Draft Tube Gas	1500	–
Conveying Gas	400	–
Purges	80	–
Product Gas	–	3000
Char	–	70
Fines	–	70
Totals	3820	3140
Closure Error	18%	

Figure 13. Overall material balance for devolatilizer test with subbituminous coal.

Gas Cleaning

Particulate removal is equally important from the environmental viewpoint and from the viewpoint of turbine protection. There are two cleanup systems under consideration. The first or preferred method is hot gas particulate removal at 1600° F by cyclones and sandbed filters. A second is the use of wet scrubbers at low temperatures. Lab evaluations of commercially available cyclones indicate that collection efficiencies are inadequate in the 0 to 6 micron range for most conventional cyclones. A special tangential jet device has on a lab

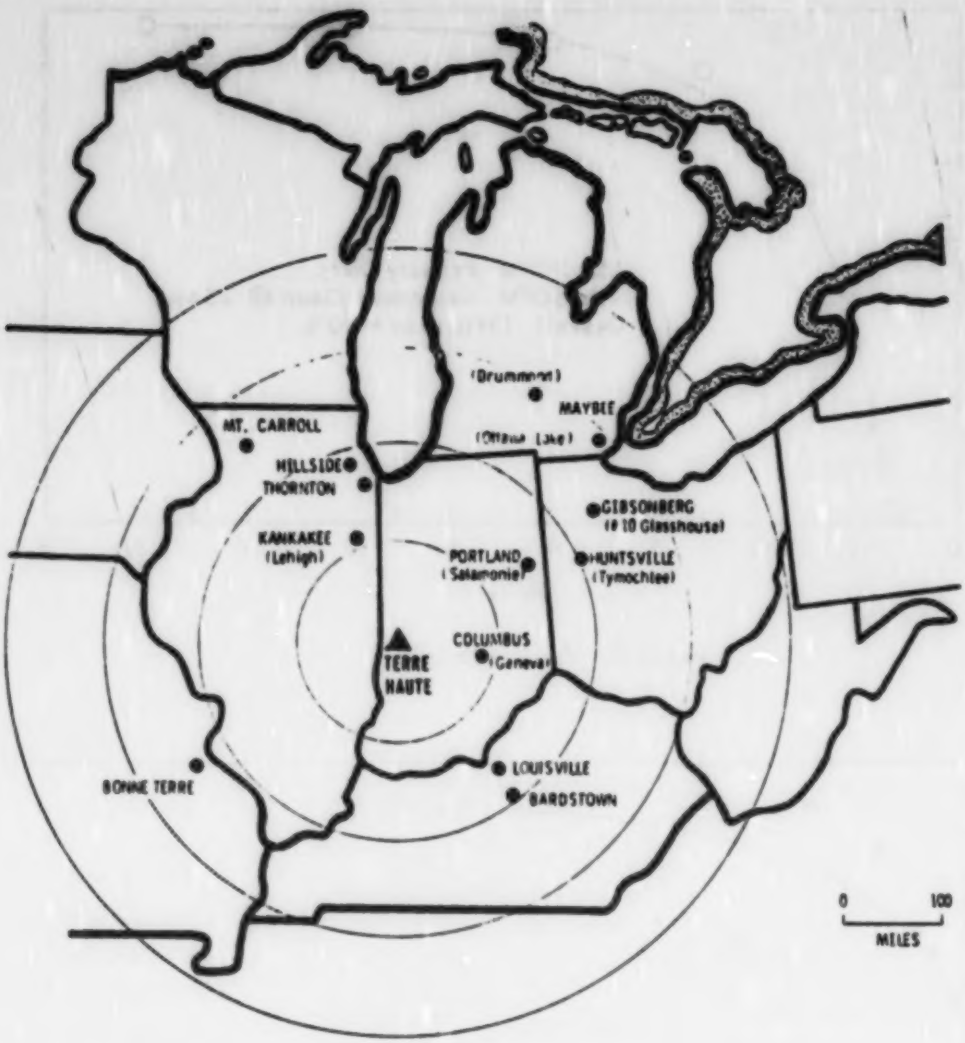

MT. CARROLL
HILLSIDE
THORNTON
KANKAKEE
(Lehigh)
(Drummond)
MAYBEE
(Ottawa Lake)
GIBSONBERG
(#10 Glasshouse)
PORTLAND
(Salamonie)
HUNTSVILLE
(Tymochtee)
COLUMBUS
(Geneva)
TERRE
HAUTE
BONNE TERRE
LOUISVILLE
BARDSTOWN
0
100
MILES

Figure 14. Location of dolomite supplies.

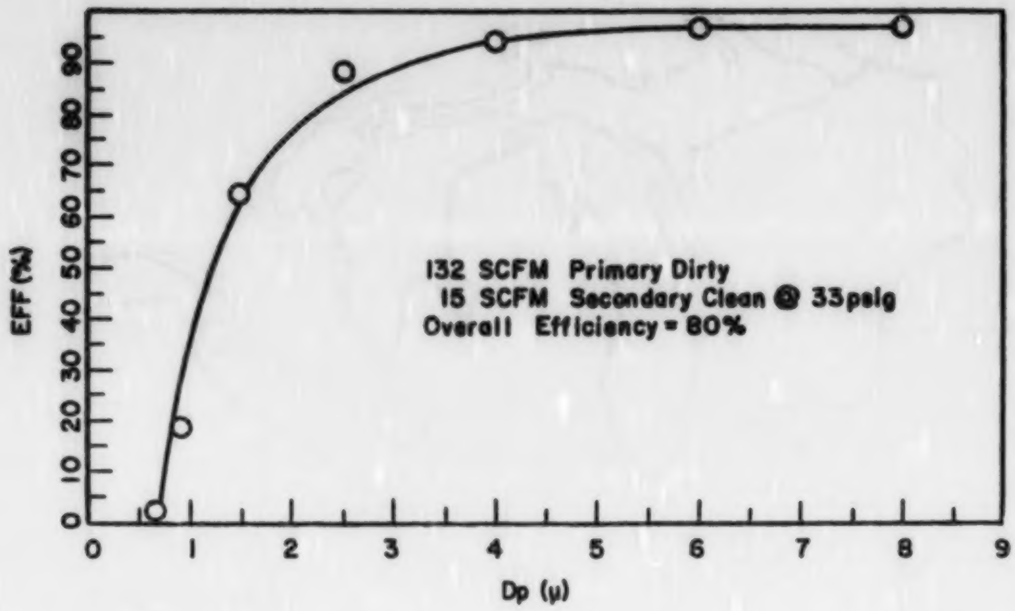


Figure 15. Tan-jet efficiency.

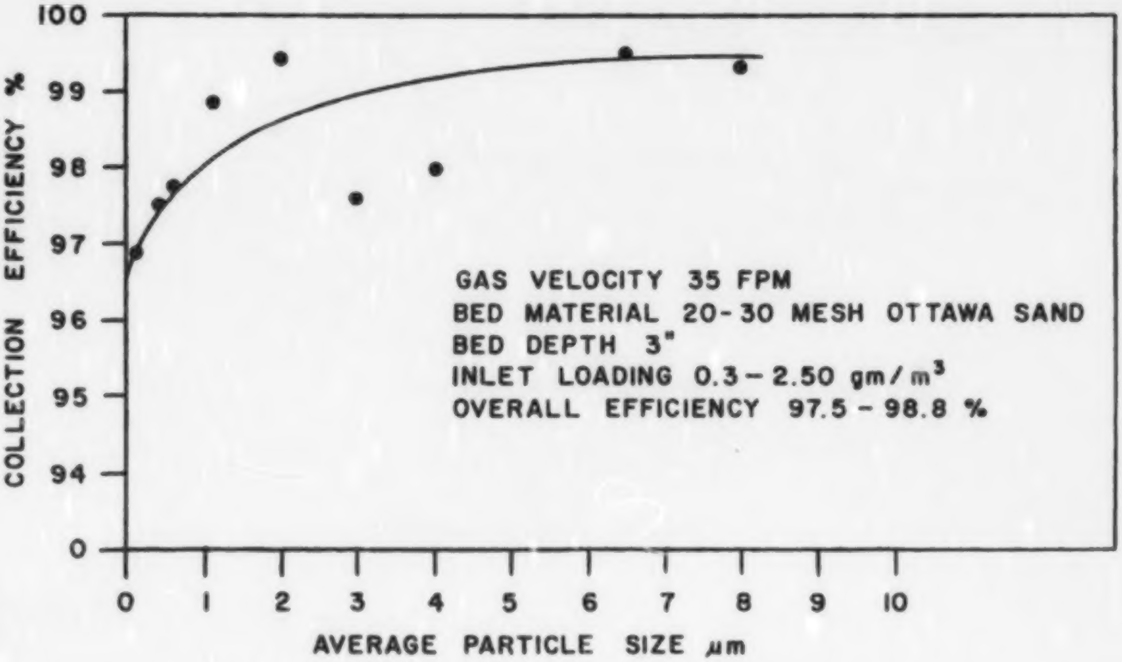


Figure 16. Dust collection on a granular bed filter.

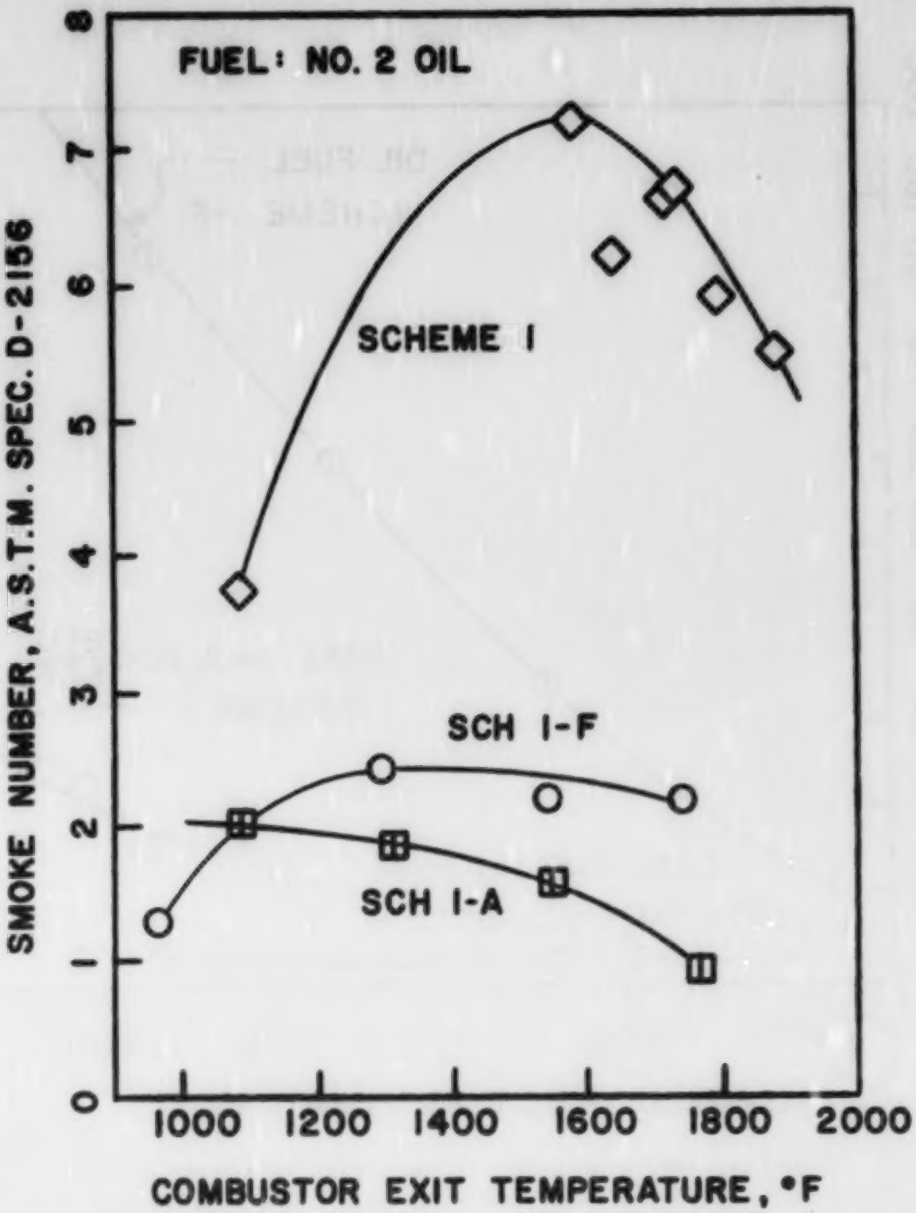


Figure 17. The effect of heating value on CO emissions for low Btu coal gas.

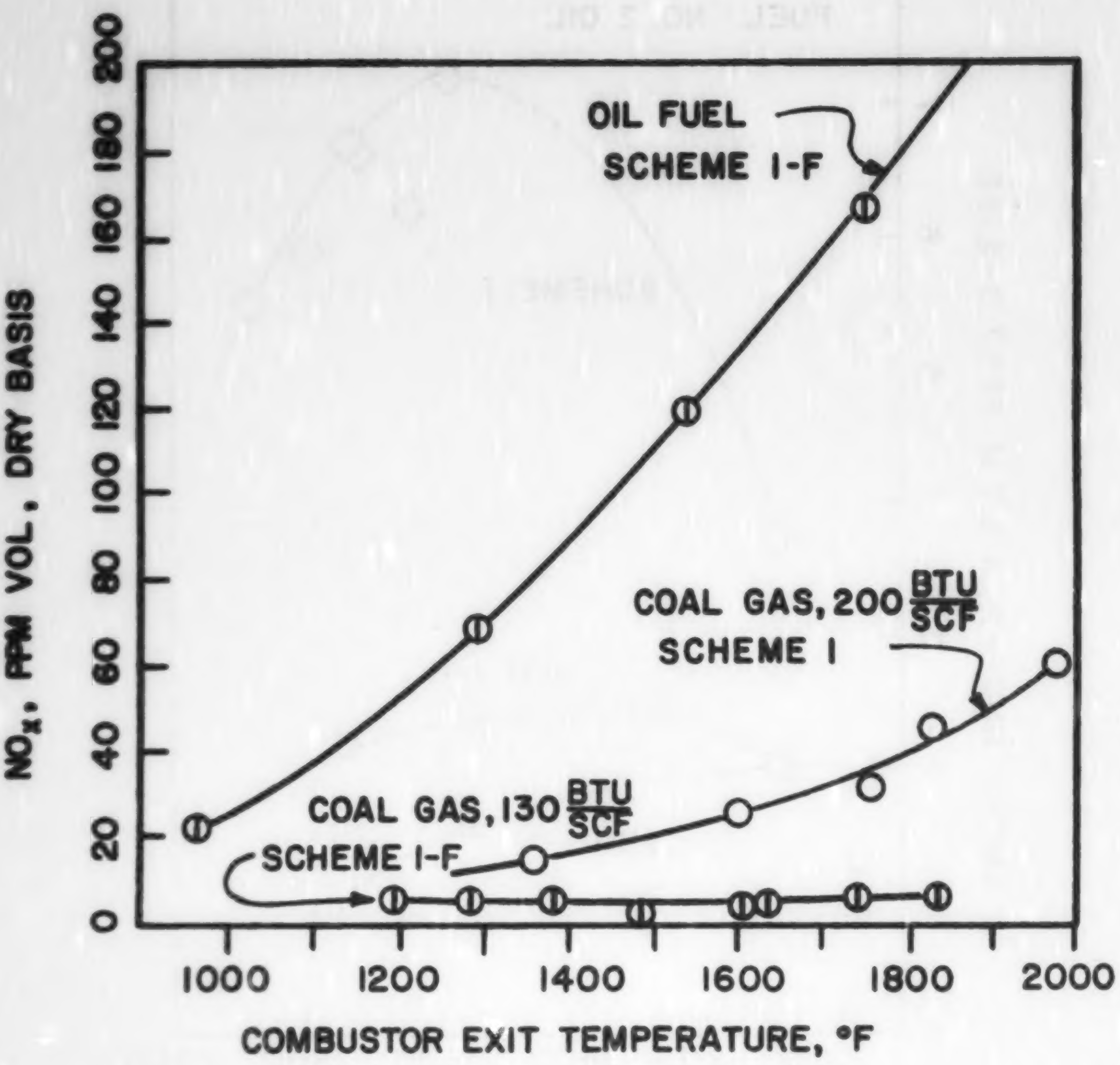


Figure 18. Comparison of NO_x emissions from the combustion of distillate oil, and low heating value coal gas of 130 and 200 Btu/Scf.

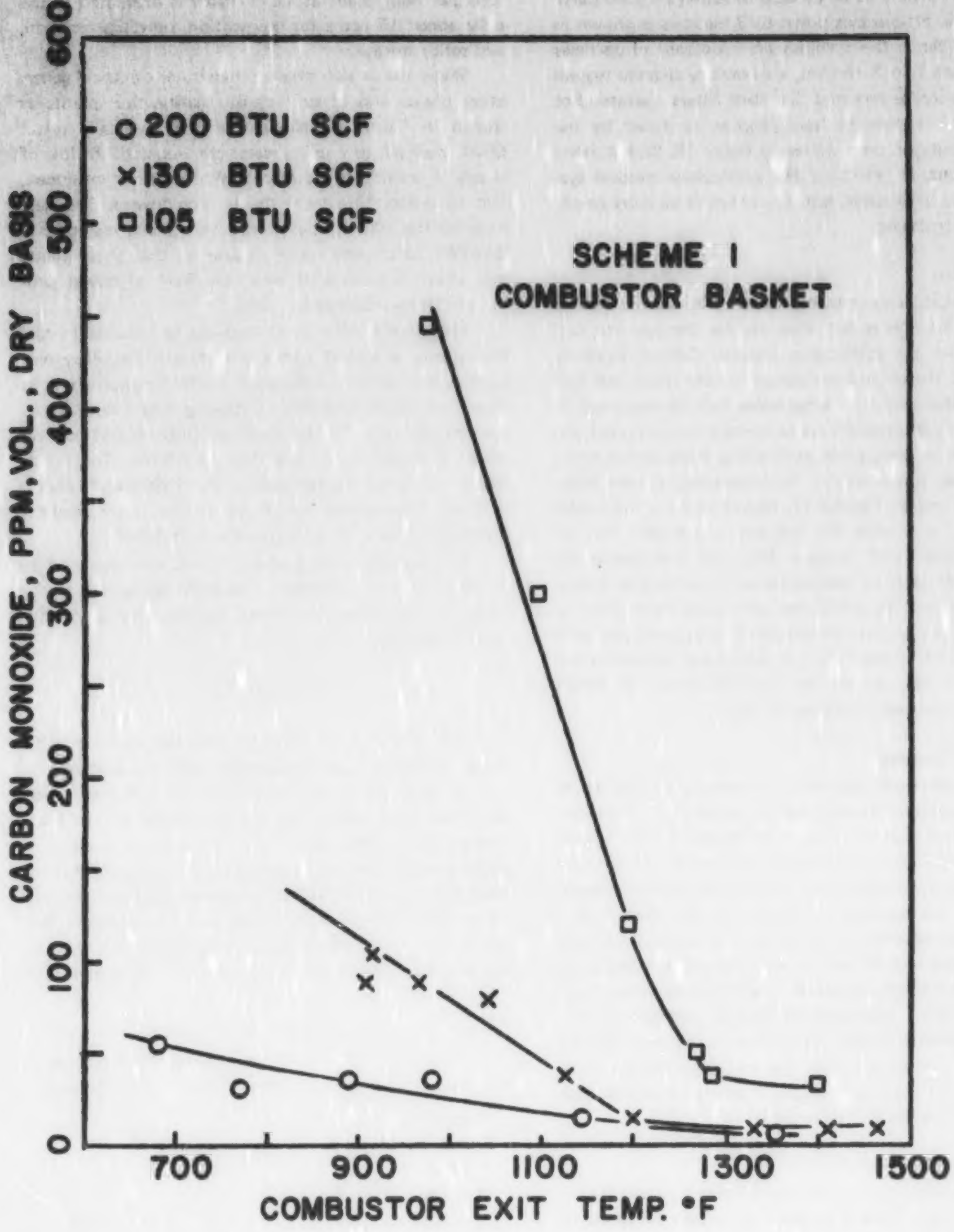


Figure 19. Smoke emission—original coal gas combustor and two low smoke versions.

scale, been shown to be capable of achieving good particle removal efficiencies down to 3 microns as shown in figure 15. Since the turbines are intolerant of particles greater than 1 to 3 microns, a secondary cleanup system will probably be required. Sandbed filters operated hot at 1600° F appear to have promise as shown by the recent results of tests shown in figure 16. With further development, an adequate hot particulate removal system should be feasible, but may prove to be more costly than wet scrubbing.

Combustion

The standard combustion basket for the gas turbine fired on fuel oil is not adequate for the low-Btu fuel produced in the gasification process. Current work on combustor design and evaluation in both small- and full-scale experiments is directed toward the development of a design which provides stable combustion at partial and full-load flow rates while minimizing emissions of nitrogen oxides, sulfur oxides, hydrocarbons, carbon monoxide and smoke. Figures 17, 18, and 19 show the results of recent tests with the full-scale combustor for the Westinghouse 501D turbine. NO_x, CO, and smoke are kept within present environmentally acceptable limits. These tests will be continued with gases formulated to simulate the low-Btu coal-derived fuel gas and later with gas produced in the PDU. Of particular concern is the amount of NH_3 in the gas, not yet measured, which could be converted to additional NO_x.

Turbine Expansion

A fundamental concern to all programs utilizing gas turbines with coal-derived fuel is the erosion, corrosion, and chemical deposition of materials on turbine blades. A substantial effort is underway to define turbine tolerance to contaminants and particulates. Alkali metals, halogens, and particulates greater in size than 1 to 3 microns are potentially damaging. The control methods being studied include the use of low alkali-releasing dolomites, addition of chemicals to the fuel to prevent sulfate deposition, adequate particulate removal as discussed previously, and adsorbtion of harmful species prior to introduction into the turbine. Whereas these studies are in their early stages, it appears that adequate turbine protection will be feasible.

Resource Utilization

The low-Btu gasification/combined-cycle plants contemplated here have a marked advantage in terms of resource use over conventional fossil plants if predictions of operating efficiencies are born out in practice. In addition, land use is relatively small because the system is operated at a pressure of 225 psig. For example, the 50 tons per hour plant at Terre Haute is estimated to use only about 15 acres for gasification, power generation, and solids storage.

Water use is also smaller than other electrical generating plants and other high-Btu gasification plants as shown in figure 20. Nuclear reactors typically reject 6500 Btu/kWh to cooling water circuits, with the loss of nearly 7 pounds of water per kWh of power produced, due to evaporation from the cooling towers. The best large central station coal fired power plants reject 5000 Btu/kWh to cooling water circuits so that these plants lose about 5 pounds of water per kWh of power produced due to evaporation losses.

The present day integrated gas turbine/steam turbine plants using fuel from a low-Btu gasification system such as that under development by Westinghouse would reject only 2000 Btu/kWh to cooling water, resulting in a water consumption for both gasification and cooling tower evaporation of less than 3 lb/kWh. The much higher efficiency gas turbines of the 1980's with 2600° F inlet temperatures could reduce the water requirements to as low as 2 lb/kWh in the next decade.

In contrast, coal gasification systems designed to produce synthetic methane or pipeline gas require on the order of ten times the water makeup that a low-Btu gasifier requires.

CONCLUSION

The Westinghouse process promises to be an efficient, economical, and environmentally acceptable process for generating electricity from coal. A number of questions exist concerning technical problems and environmental considerations. These are being attached in a well-balanced program consisting of lab-scale experiments, pilot scale (PDU) development tests, and analytical studies. The program is still in its early stages, but results thus far are encouraging and give promise that the technical, economic, and environmental requirements of

	Pounds water per kWh	Pounds water per lb/coal
Nuclear electric	7	–
Conventional fossil electric	5	–
Low Btu gasification, combined cycle	2.3	0.44
High Btu gasification	–	5.0

Figure 20. Water utilization estimates.

the system can be met in the design of the generating plant to be built for Public Service of Indiana.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of coworkers on this program who furnished material for this paper: D. H. Archer, J. R. Hamm, B. W. Lancaster, E. F. Sverdrup, R. M. Chamberlin, D. L. Keairns, J. L. Chen, J. P. Morris, E. P. O'Neill, C. H. Peterson, W. C. Yang, P. Cherish, L. H. Grob, P. J. Margaritis, L. K. Rath, R. D. Shah, S. S. Kim, E. J. Chelen, M. J. Arthurs, J. E. Macko, R. B. Mangold, W. R. Miller, D. E. Rudisill and S. P. Tendulkar.

ROLE OF GASIFIER PROCESS VARIABLES IN EFFLUENT AND PRODUCT GAS PRODUCTION IN THE SYNTHANE PROCESS

M. J. Massey, D. V. Nakles, A. J. Forney, and W. P. Haynes*

Abstract

During steam-oxygen gasification of coal by the Synthane Process and others, substantial quantities of foul condensate and sulfur-bearing char and tar are produced. Little is known quantitatively either about steady state rates of production of various gasifier effluents or about the relative effects of process variables in coal gasification on the types and rates of their production. Utilizing the Pittsburgh Energy Research Center's (PERC) 4-inch diameter Synthane gasifier, a series of 19 tests on North Dakota lignite were conducted to study quantitatively the nature of effluent production and the various gasifier process variables which affect it. Process variables, e.g., fresh coal heatup rate, product gas residence time, reaction temperature, and the extent of gas-solid contacting were varied by altering the fresh coal injection position within the gasifier. Among the major findings were: (1) effluent production rates, viz., quantities of hydrocarbon condensate and water soluble contaminants, very significantly with time from gasifier startup to the attainment of steady state operation; (2) steady state effluent composition and production rates are affected strongly by changes in coal injection geometry; (3) at least two mechanisms appear to be responsible for observed variations in the levels of production of various effluents; and (4) modified gasifier design offers at least a complement and quite possibly an alternative to large-scale conventional treatment of gasifier effluents.

INTRODUCTION

During steam-oxygen gasification of coal by the Synthane Process and others, substantial quantities of foul condensate and sulfur-bearing char and tar are produced. Little is known quantitatively either about steady state rates of production of various gasifier effluents or about the relative effects of process variables in coal gasification on the types and rates of their production. Utilizing the Pittsburgh Energy Research Center's (PERC) 4-inch diameter Synthane gasifier, the present experimental program was initiated to study quantitatively the nature of effluent production and the various gasifier process variables which affect it. Included in the investigation were studies of:

(1) rates of production of various gasifier effluents as a function of time from gasifier startup to shutdown;
(2) effects of selected process variables on the rate of production of various effluents;
(3) associated effects of changes in these variables on yields of total product gas and equivalent methane (methane plus twice the ethane production); and
(4) impacts of changes in selected process variables on the composition and physical properties of char and tar produced.

To minimize experimental complications, noncaking North Dakota lignite coal was used exclusively in the 19 gasification tests conducted during this investigation. Process variables, e.g., fresh coal heatup rate, product gas residence time, reaction temperature, and the extent of gas-solid contacting, were varied by altering the fresh coal injection position, and their impact on effluent production was monitored. During any given test, condensible hydrocarbons and contaminated water were separated from raw producer gas continuously; at 45-minute intervals, accumulated aqueous and hydrocarbon condensate were withdrawn from condensers, weighed, and sampled for analysis. Noncondensible product gas production and composition were monitored at 30-minute intervals throughout each run. Gasifier char was collected in a batch reservoir during each run and sampled once for analysis.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Gasifier Configuration and Effluent Sampling Apparatus

In support of its Synthane process development program, the Pittsburgh Energy Research Center (PERC) has since 1960 been conducting coal gasification experiments in a 4-inch diameter fluid bed reactor. A flow diagram illustrating the conventional equipment train for these tests is presented in figure 1. Fresh coal is injected into the gasifier under pressure (40 atm) at the rate of about 25 lbs/hr; reactant gases (steam and oxygen) are introduced at the base of the gasifier. Unreacted solids

---

*Michael J. Massey is Assistant Professor, Chemical Engineering and Public Affairs, Carnegie-Mellon Universtiy, Pittsburgh, Pennsylvania. David V. Nakles is Chemical Engineer, Pittsburgh Energy Research Center and a graduate student at Carnegie-Mellon University. Albert J. Forney is Research Supervisor; William P. Haynes is Supervisory Chemical Engineer, Pittsburgh Energy Research Center.

Preceding page blank

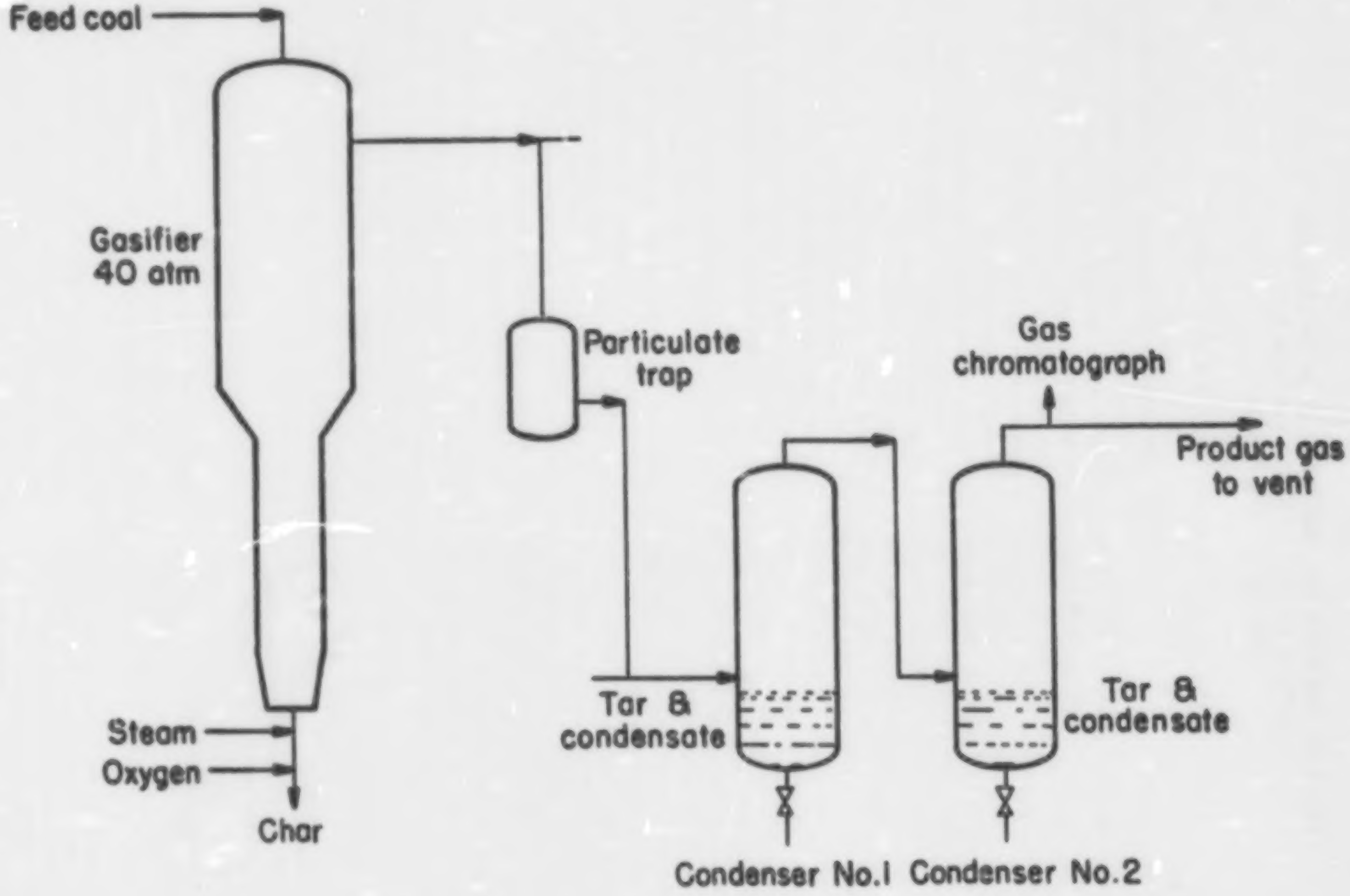

Feed coal
Gasifier
40 atm
Steam
Oxygen
Char
Particulate
trap
Tar &
condensate
Gas
chromatograph
Product gas
to vent
Tar &
condensate
Condenser No.1
Condenser No.2

Figure 1. Basic laboratory scale equipment train for the batchwise collection of aqueous and liquid hydrocarbon effluents from the Synthane gasifier.

(char) are discharged from the base of the reactor to a batch receiver while raw product gas is withdrawn from the top of the reactor. Following coarse particulate removal, this gas is cooled in a series of two water-jacketed condensers where high molecular weight hydrocarbons and contaminated water are condensed and collected in large batch reservoirs. Prior to venting, the composition and flowrate of noncondensible gases leaving the second condenser are measured. At the end of each test, aqueous and hydrocarbon condensates from batch reservoirs are weighed and sampled. Results of batch analyses of a large number of gasification tests with caking and noncaking coals are presented in two recent PERC reports (refs. 1,2).

As is illustrated in figure 2, the Synthane gasifier is divided into two sections, an upper carbonization zone (~6 ft) through which fresh coal free-falls and/or unreacted solids disengage from product gases, and a lower fluidized bed zone (~6 ft). In the present experimental program, fresh lignite coal was injected into the gasifier at one of three locations: (1) the top of the carbonizer (free-fall injections); (2) approximately 1-1/3 ft into the fluidized bed (shallow bed-injections); and (3) approximately 4½ ft into the fluidized bed (deep bed-injections). Although some variation in gasifier temperature profile with coal injection position occurs (see figure 3), typical reactor temperatures range from an average of 400° to 500° C at the top of the carbonizer to 800° to 900° C at the base of the fluidized bed.

To permit periodic sampling of hydrocarbon and water condensates during the present test program, the batch condensate collection equipment shown in figure 1 was modified as shown in figure 4. Small reservoirs were attached to the base of each condenser. At regular intervals, these reservoirs were pressurized with nitrogen and filled with accumulated condenser condensate. Subsequently, each reservoir was depressurized and the contents were drained, weighed, and sampled for analysis. Gases vented during depressurization of these reservoirs were collected during one run and analyzed to determine whether condensate fractions, particularly light hydrocarbons such as benzene were being vaporized and lost. Mass spectrographic analysis of blowdown gases indicated the presence of largely N_2 and CO_2 and essentially no light hydrocarbons.

Experimental and Analytical Procedure

With the exception of the coal feeding technique, experimental procedure was standardized as much as possible from run to run. At startup, N_2 was employed as the initial fluidizing agent and reactor heat was supplied electrically. Gradually, steam and oxygen flows were increased, nitrogen flow was decreased and reactor heat requirements were met increasingly by exothermic gasification reactions. Following an initial accumulation of solids in the reactor's fluid bed, char extraction rates were varied to maintain a desired bed height. Bed temperatures were maintained largely by varying the flowrate of oxygen to the reactor. Note that both oxygen flowrate and char extraction rate were varied manually. A certain amount of the observed fluctuation in gasifier performance during a run is believed to be related to this manual control.

In each experiment, a measured quantity of cold coal was discharged at a known rate from a pressurized reservoir to the gasifier through a star feeder. In the free-fall injection runs, coal was allowed to fall by gravity from the top of the gasifier. In the shallow and deep bed-injection runs, nitrogen was utilized as a propellant to transport the coal through a standpipe from the top of the reactor to the appropriate point of injection within the fluidized bed.

From reactor startup to shutdown (typically about 6 hours), product gas samples were collected every 30 minutes. Condensates (hydrocarbon and aqueous) were collected for 1½ hours during reactor startup and at 45 minute intervals for the remainder of the run. Product gas was analyzed routinely by three independent techniques—on line gas chromatography, mass spectroscopy and laboratory gas chromatography—and the results were averaged. Condensates first were separated and weighed. Samples of water then were withdrawn and routinely analyzed for phenol, cyanide, thiocyanate, chemical oxygen demand, and total organic and inorganic carbon. Ultimate analyses, true boiling point curves and specific gravities were determined for a limited number of hydrocarbon condensate samples to characterize tar composition.

Unreacted solids (char) were discharged from the gasifier through an extractor to a pressurized receiver where they accumulated throughout a run. At the end of each run, this receiver was emptied and a batch sample of the char was collected for ultimate analysis.

Following each gasification test, hydrogen, carbon, and oxygen mass balances were determined on the basis of the known composition of the feed coal, measured steam, oxygen, and nitrogen feedrates, and the weights and compositions of collected product gas, gasifier char, and hydrocarbon/water condensates.

EXPERIMENTAL RESULTS

Five free-fall, eight shallow, and six deep bed-injection gasification tests were conducted on North Dakota lignite. Relevant operating statistics for each of these tests are presented in table 1. Time series plots of product gas and equivalent methane production rates as

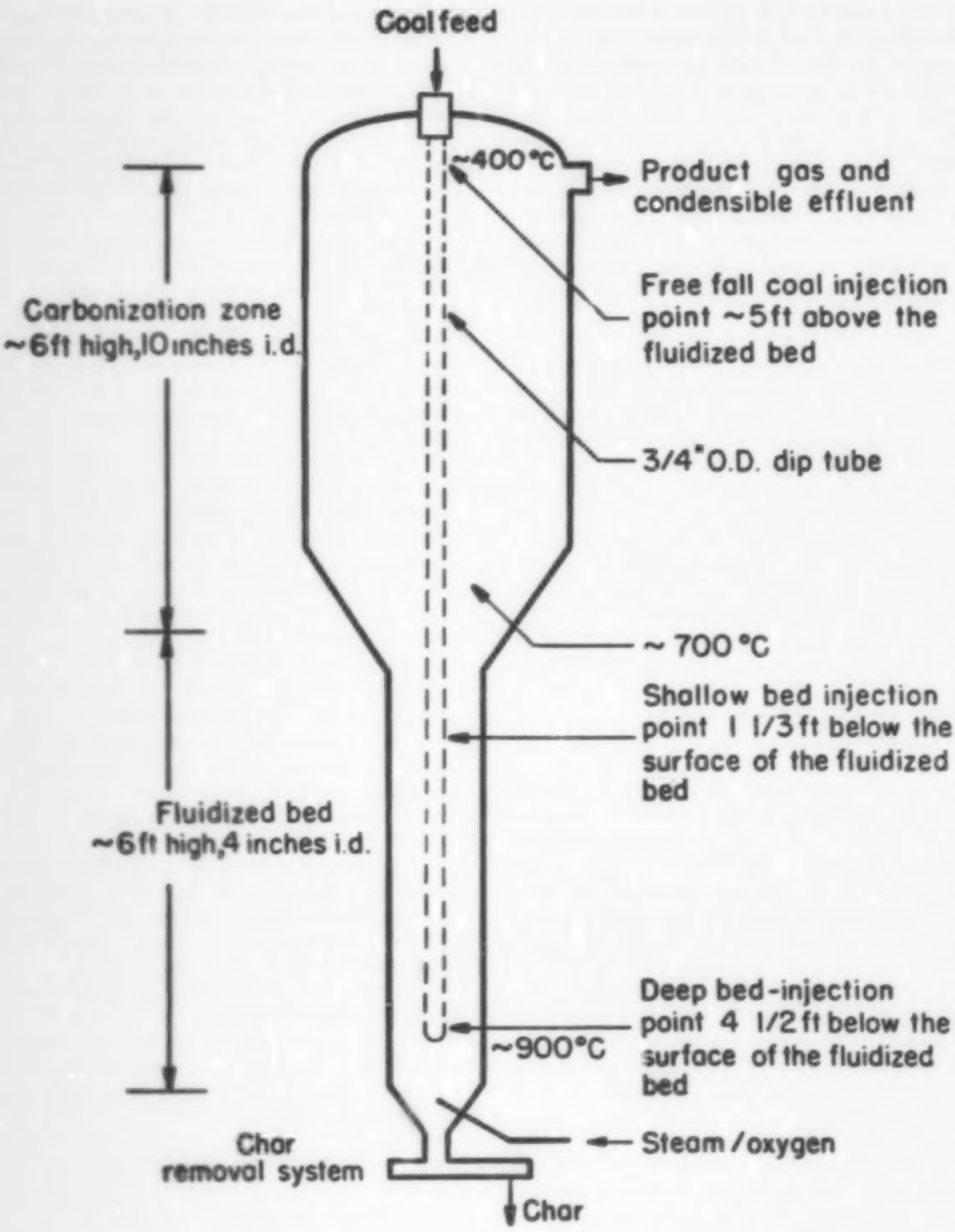

Coal feed
~400 °C
Product gas and condensible effluent
Free fall coal injection point ~5 ft above the fluidized bed
Carbonization zone ~6 ft high, 10 inches i.d.
3/4" O.D. dip tube
~ 700 °C
Shallow bed injection point 1 1/3 ft below the surface of the fluidized bed
Fluidized bed ~6 ft high, 4 inches i.d.
Deep bed-injection point 4 1/2 ft below the surface of the fluidized bed
~900°C
Char removal system
Steam / oxygen
Char

Figure 2. Basic configuration and coal feed locations of Synthane gasifier.

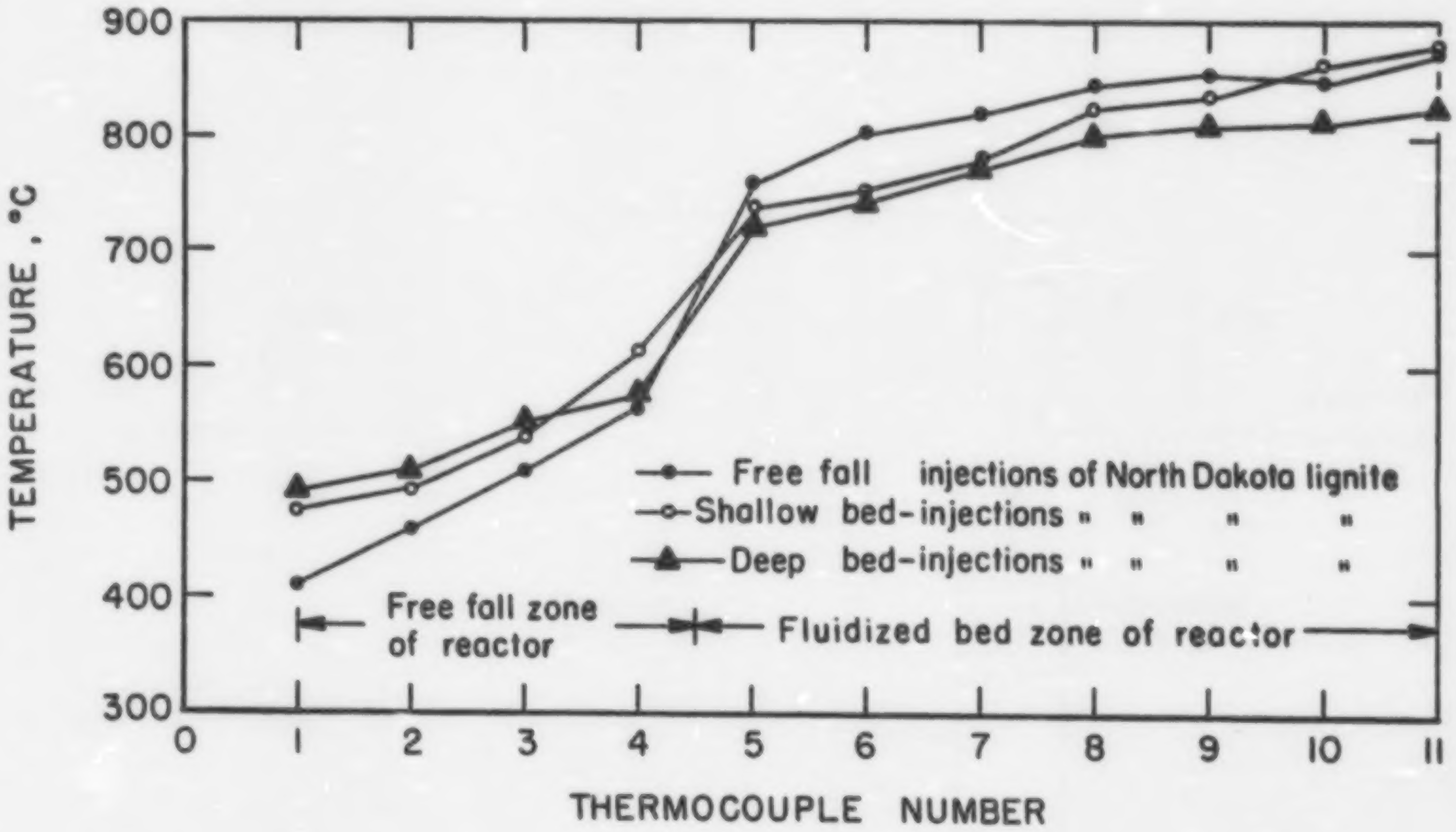


Figure 3. Variations in gasifier axial temperature profiles with coal injection location.

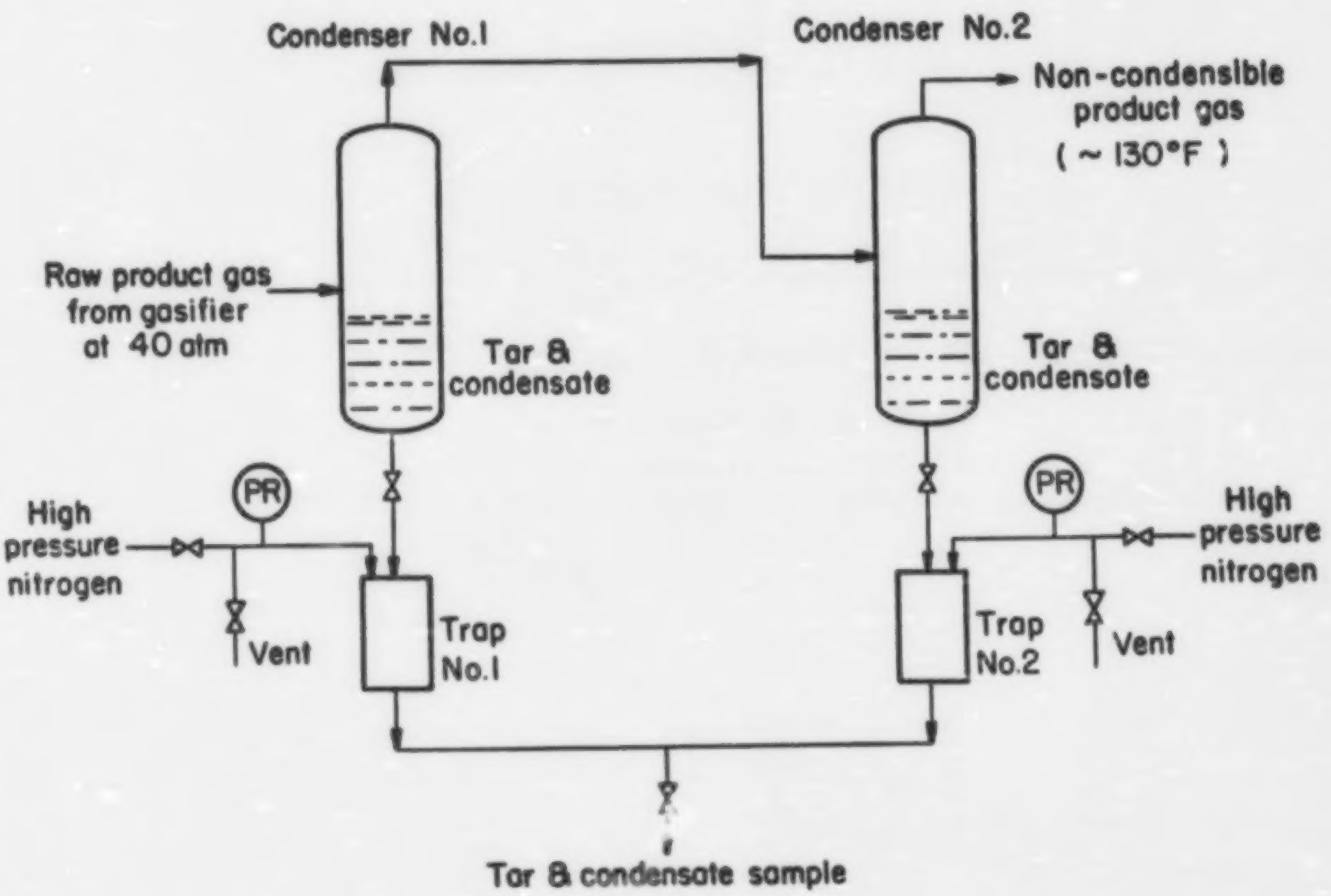

Condenser No.1
Condenser No.2
Non-condensible product gas
(~ 130°F)
Raw product gas from gasifier at 40 atm
Tar & condensate
Tar & condensate
PR
High pressure nitrogen
Vent
Trap No.1
PR
High pressure nitrogen
Trap No.2
Vent
Tar & condensate sample

Figure 4. Apparatus for intermittent sampling of tar and condensates produced during the gasification of coal.

Table 1. Operating and product gas statistics, series of steam-oxygen gasification trials: free-fall, shallow and deep bed-injections of North Dakota Lignite coal

Trial	Date	Gasifier Reactant Feedrates, lb/hr			Fluid Bed Temp., °C			Reactor Operating Time, hrs		% Reactant Conversion		Residual Coal Anal., wt %		Gas Production, scf/lb C gasified	
		Coal	Steam	Oxygen	Bottom	Average	Top	Total	Steady State^a	Steam	Carbon	Vol	Ash	Equiv CH4^b	Product Gas^c
FREE FALL INJECTION OF LIGNITE COAL															
CHFFL-131	08-13-76	34.14	30.41	7.40	857	836	806	5.30	2.0	33.7	84.1	23.4	7.6	5.40 ± .36	34.94 ± 1.00
CHFFL-132	08-20-76	33.16	30.16	6.77	866	837	799	6.00	2.5	35.8	86.9	13.9	7.0	5.06 ± .29	32.97 ± .87
CHFFL-133	08-26-76	33.10	30.10	6.77	871	833	740	6.00	3.0	36.3	90.3	12.3	9.0	3.99 ± .26	33.11 ± .08
CHFFL-134	08-28-76	36.96	30.10	7.02	875	831	733	5.73	2.5	39.6	82.1	22.4	7.3	6.06 ± .09	30.02 ± 1.70
CHFFL-135	08-30-76	33.70	39.10	7.32	873	833	717	5.00	3.0	36.4	70.8	13.7	7.3	5.33 ± .30	34.36 ± 1.08
SHALLOW BED-INJECTION OF LIGNITE COAL															
CHFFL-123	07-02-76	37.86	36.10	6.33	839	805	743	4.97	3.5	33.3	72.8	12.7	8.5	6.46 ± .40	32.26 ± 2.50
CHFFL-124	07-08-76	36.73	36.10	6.77	796	790	731	3.33	4.0	36.0	74.6	18.4	6.6	6.27 ± .94	30.30 ± 3.30
CHFFL-125	07-17-76	36.19	40.44	6.95	864	784	718	3.30	3.5	30.0	76.1	24.4	7.5	6.30 ± .14	31.21 ± .95
CHFFL-126	07-19-76	36.38	30.71	6.95	831	786	729	5.50	3.5	28.5	77.7	13.9	7.3	6.60 ± .41	29.66 ± 1.00
CHFFL-127	07-23-76	34.48	30.41	5.80	836	776	703	6.00	3.5	26.3	81.2	12.2	8.2	5.70 ± .23	30.20 ± 1.30
CHFFL-136	09-04-76	33.60	30.21	6.38	858	784	733	6.00	3.0	37.8	80.8	13.8	7.0	5.64 ± .17	31.37 ± 1.00
CHFFL-137	09-06-76	33.88	29.35	7.73	877	786	716	6.00	3.0	33.4	87.3	18.7	7.3	5.12 ± .11	30.86 ± .75
CHFFL-138	09-12-76	33.44	30.26	7.13	868	792	712	6.00	3.5	36.1	86.1	18.3	8.1	5.39 ± .75	28.30 ± 3.30
DEEP BED-INJECTION OF LIGNITE COAL															
CHFFL-143	10-08-76	33.48	39.11	7.67	706	720	716	3.41	1.3	13.6	68.9	23.1	7.4	6.72 ± 1.60	41.27 ± 3.70
CHFFL-144	10-15-76	26.38	39.11	7.86	827	707	731	6.40	3.0	30.8	73.8	16.1	8.0	5.06 ± .39	23.70 ± 3.39
CHFFL-146	11-04-76	23.52	39.16	9.08	809	705	720	5.80	3.8	30.3	67.9	16.1	6.7	5.71 ± .30	26.98 ± 1.00
CHFFL-147	11-06-76	26.88	30.11	9.37	819	729	717	5.30	1.5	38.1	61.9	11.0	6.4	5.36 ± .24	36.26 ± .95
CHFFL-148	11-08-76	33.78	30.11	9.43	806	735	729	5.80	3.6	10.6	66.3	10.7	6.4	5.93 ± .38	37.06 ± 1.30
CHFFL-149	11-12-76	33.70	39.11	9.18	776	730	711	5.07	2.5	30.9	66.0	16.9	6.5	3.40 ± .43	38.96 ± .40

(a) That period during which the product gas H_2 concentration was approximately constant.

(b) Equiv. CH_4 = sum of SCF of CH_4 plus twice the SCF of C_2H_4.

(c) Product Gas = sum of SCF of CH_4, C_2H_4, H_2, and CO.

a function of time for individual tests are presented in figures 5 and 6, respectively. Carbon, hydrogen, and oxygen mass balances for each test are summarized in figure 7. As is apparent from this figure, material was consistently lost during each experiment conducted. The closest approximation to closure of a mass balance occurred during the six deep bed-injection tests.

Aqueous Effluent Production

Time series measurements of phenol, chemical oxygen demand, and total organic and inorganic carbon contents of aqueous condensates are presented in figures 8-11, respectively. Similar measurements of thiocyanate concentrations are presented in table 2; cyanide measurements, though taken routinely, rarely exceeded 0.01 ppm and, therefore, were not tabulated. Data in each figure are grouped according to coal injection geometry, viz., free-fall, shallow, and deep bed-injection. Note that with the exception of inorganic carbon measurements, all the data reported indicate major reductions in effluent production as a function of both time and depth of coal injection. Consistent inorganic carbon contents were anticipated; they reflect the presence of dissolved CO_2 in basic (pH 9) condensate. At steady state, measured phenol production rates range from a high of 12 lbs/ton coal, MAF (free fall injections) to a low of < 0.5 lbs/ton coal, MAF or equivalently less than 30 ppm (deep bed-injections). Similarly, chemical oxygen demands range from a high of ~80 lbs/ton coal, MAF to a low of ~2.5 lbs/ton coal, MAF and total organic carbon contents range from a high of ~21 lbs/ton coal, MAF to a low of ~2 lbs/ton coal, MAF. Thiocyanate production rates range from a high of ~0.045 lbs/ton coal, MAF (free-fall injections) to a low of less than 0.017 lbs/ton coal, MAF (deep bed-injections), the limiting sensitivity of the measurement technique employed.

Recent analytical work carried out at PERC on aqueous condensates from a range of Illinois No. 6 gasification tests (ref. 3) reflect the trends toward decreased phenol production with increased depth of fresh coal injection reported here in figure 8. Concentrations of selected compounds measured in condensates from two free-fall and three shallow bed-injection tests with Illinois No. 6 coal and reported in reference 3 are summarized in table 3.

In contrast to the considerable scatter evident in previously reported effluent production data (ref. 12), note that in the present series of experiments, individual data for runs at constant coal injection geometry are substantially reproducible. Also, note that in the particular case of free-fall injection tests, steady state production rates of all the effluents measured actually exceed those at gasifier startup. This result was not anticipated; an initial surge in effluent production followed by a decline toward a reduced production rate at steady state had been expected. The expected pattern of production with time did occur in the shallow and deep bed-injection tests.

Ammonia Production

Time series data on ammonia production rates were not collected in the present experimental program. However, at least one measurement of ammonia content of aqueous condensate was made during all but two of the tests run. In contrast to the patterns of other major constituents of gasifier condensate, ammonia production was not influenced significantly by variations in coal injection geometry. Within the accuracy of the data available, ammonia production averaged 15-20 lbs/ton coal, MAF. This yield is substantially greater than the approximately 6-8 lbs NH_3/ton coal, MAF typically produced in byproduct coking (ref. 4).

Char Production and Composition

Statistics on char production and composition are summarized in table 4 for free-fall, shallow, and deep bed-injections of coal.* From free-fall to shallow to deep bed-injections, there is a distinct trend towards increased volumes of char having progressively higher carbon, hydrogen, oxygen, and nitrogen contents, lower ash contents, and higher heating values. Char sulfur levels, though stable and well below the Federal New Source Performance Standard of 1.2 lbs SO_2/MMBTU for shallow and free-fall coal injection runs, increase sharply for deep bed-injection runs. These data indicate clearly that, with deepening injection, increasing amounts of feed coal exit the reactor prematurely through the char extractor, reducing overall levels of char conversion. This is a direct result of the particular injection geometry employed in these experiments (see figure 2), and could be altered with proper modification of the reactor injection system.

Hydrocarbon Condensate (Tar) Production

Tar production rates for each of the 19 experiments conducted are presented as a function of time in figure 12. Grouped according to coal injection geometry, these data indicate that: (1) with the exception of free-fall coal injection runs, tar production declines with time from an initially high rate to a reduced rate at steady state; and (2) steady state tar production levels fall rapidly as coal is injected deeper into the fluidized bed portion of the reactor. As with the previously cited aqueous effluent production data, steady state tar production levels in the free-fall injection tests actually exceed those observed during gasifier startup. Measured

---

*Detailed data for individual experiments are provided in reference 2.

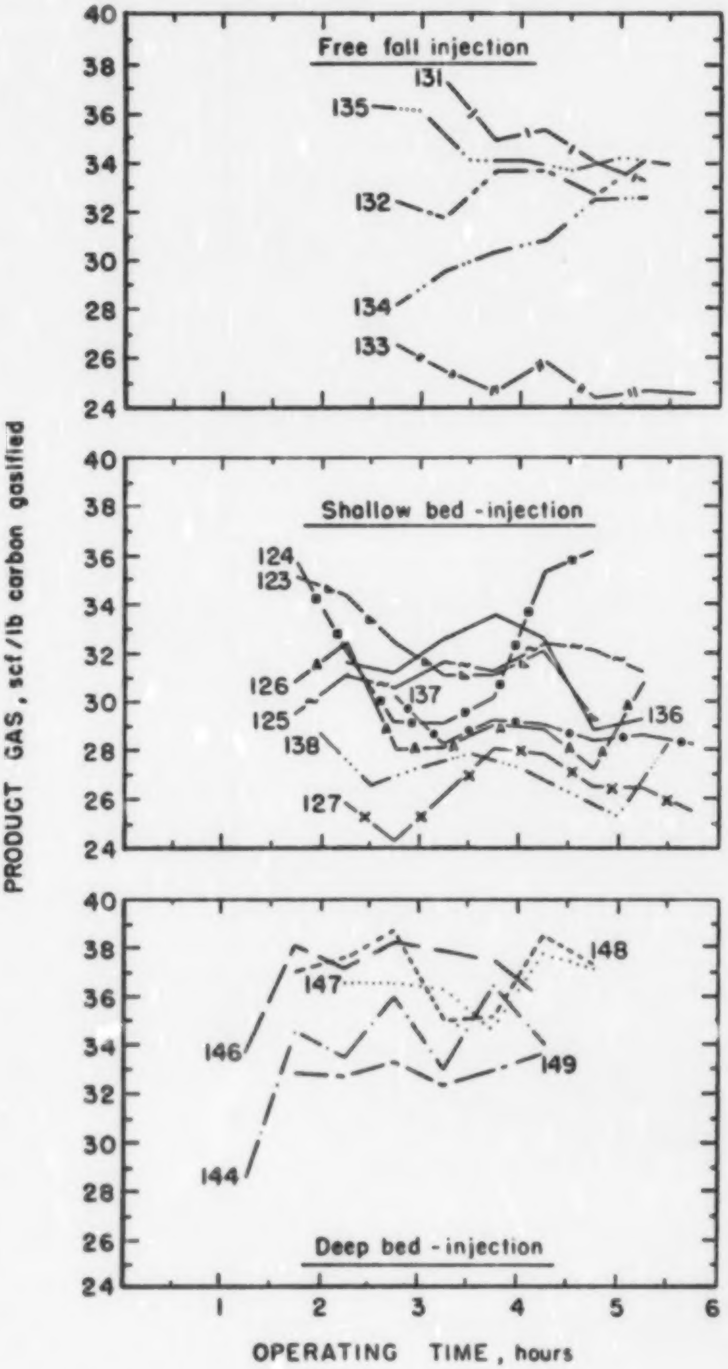


Figure 5. Product gas production versus time: gasification of North Dakota lignite.

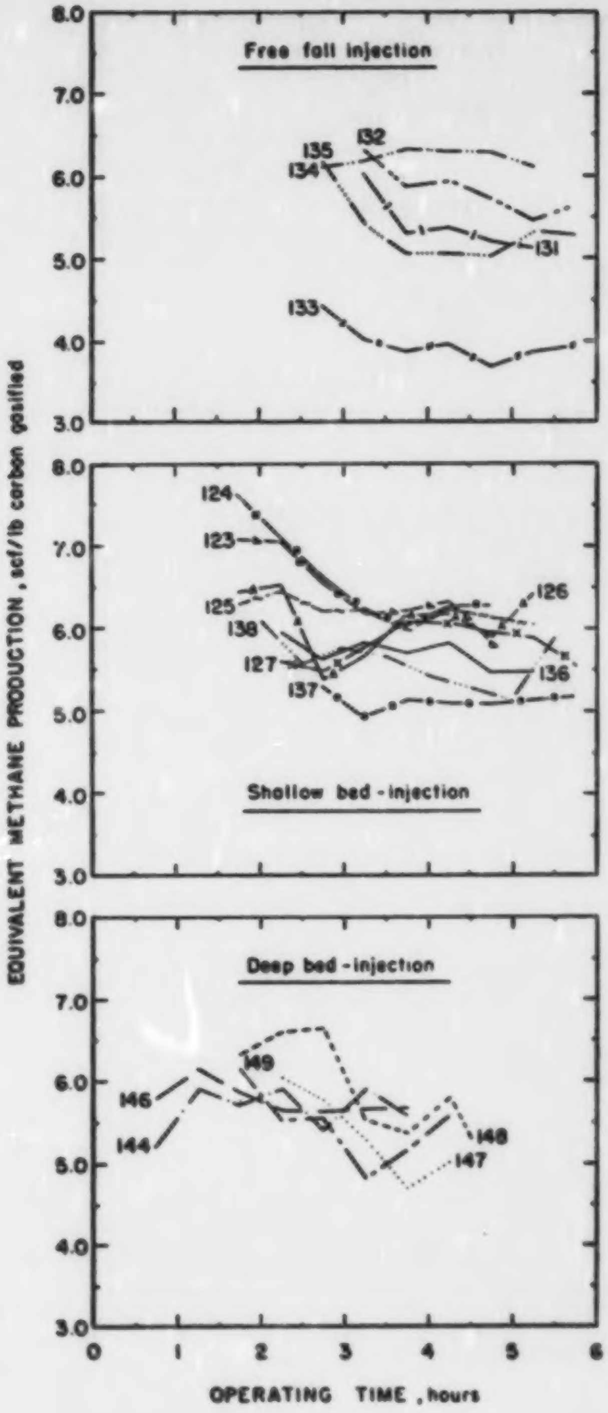


Figure 6. Equivalent methane production versus time: gasification of North Dakota lignite.

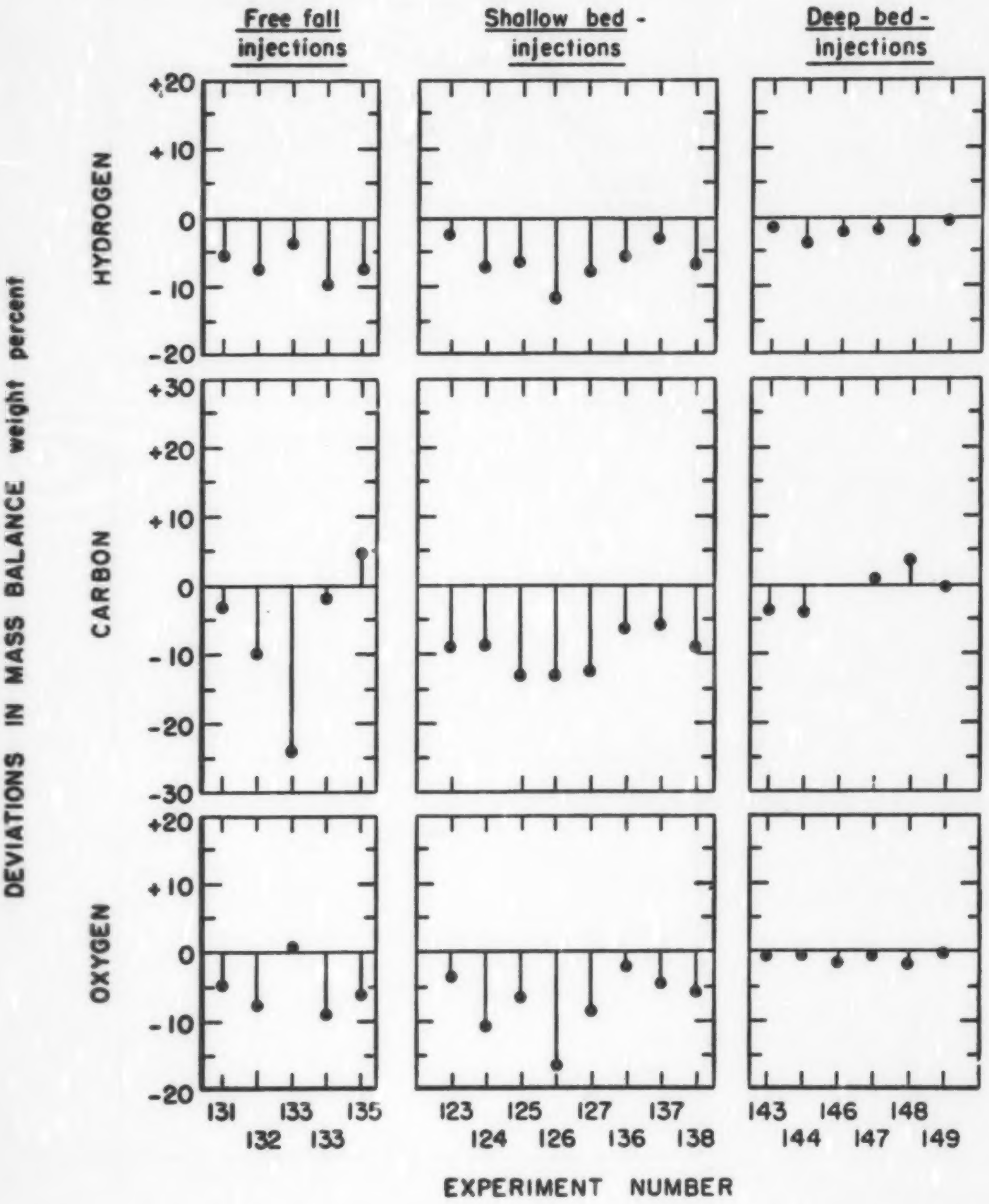


Figure 7. Hydrogen, carbon, and oxygen mass balances: gasification of North Dakota lignite.

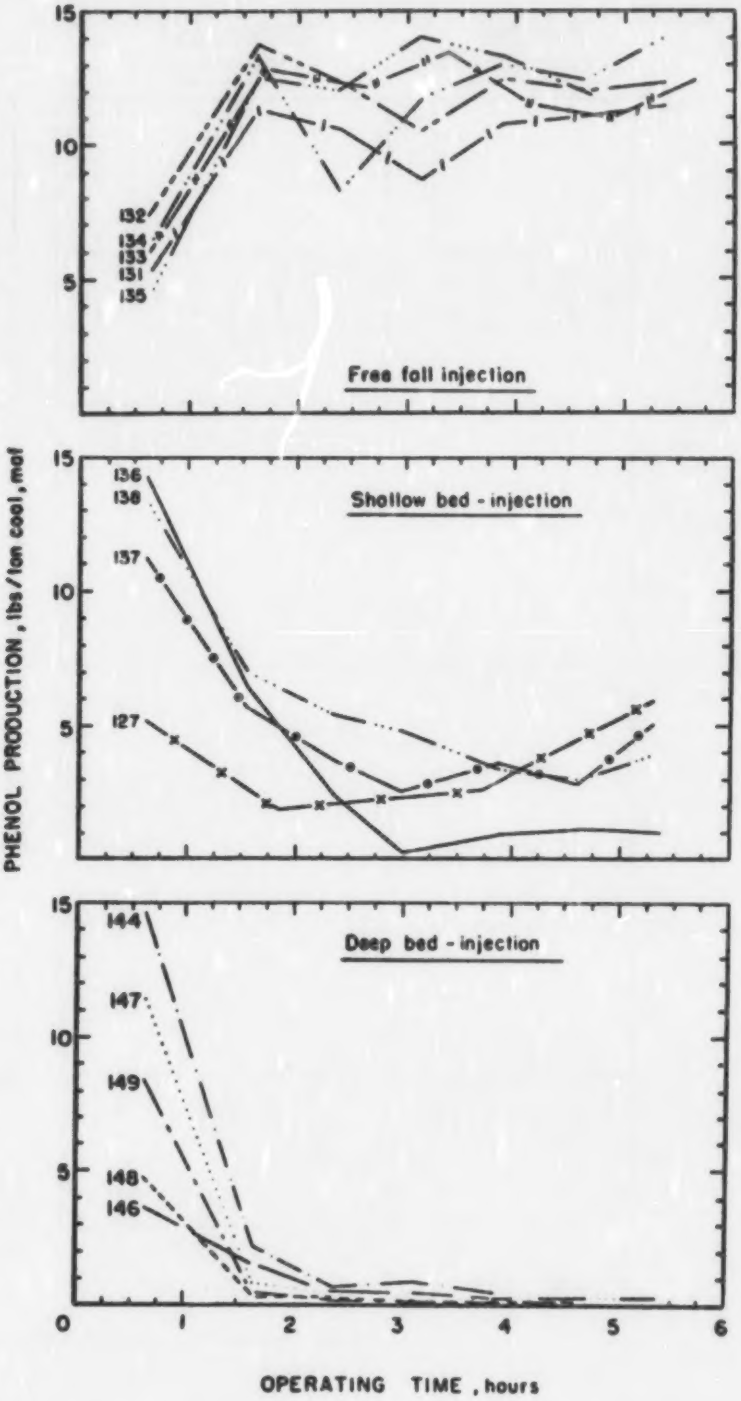


Figure 8. Phenol in byproduct water versus time: gasification of North Dakota lignite.

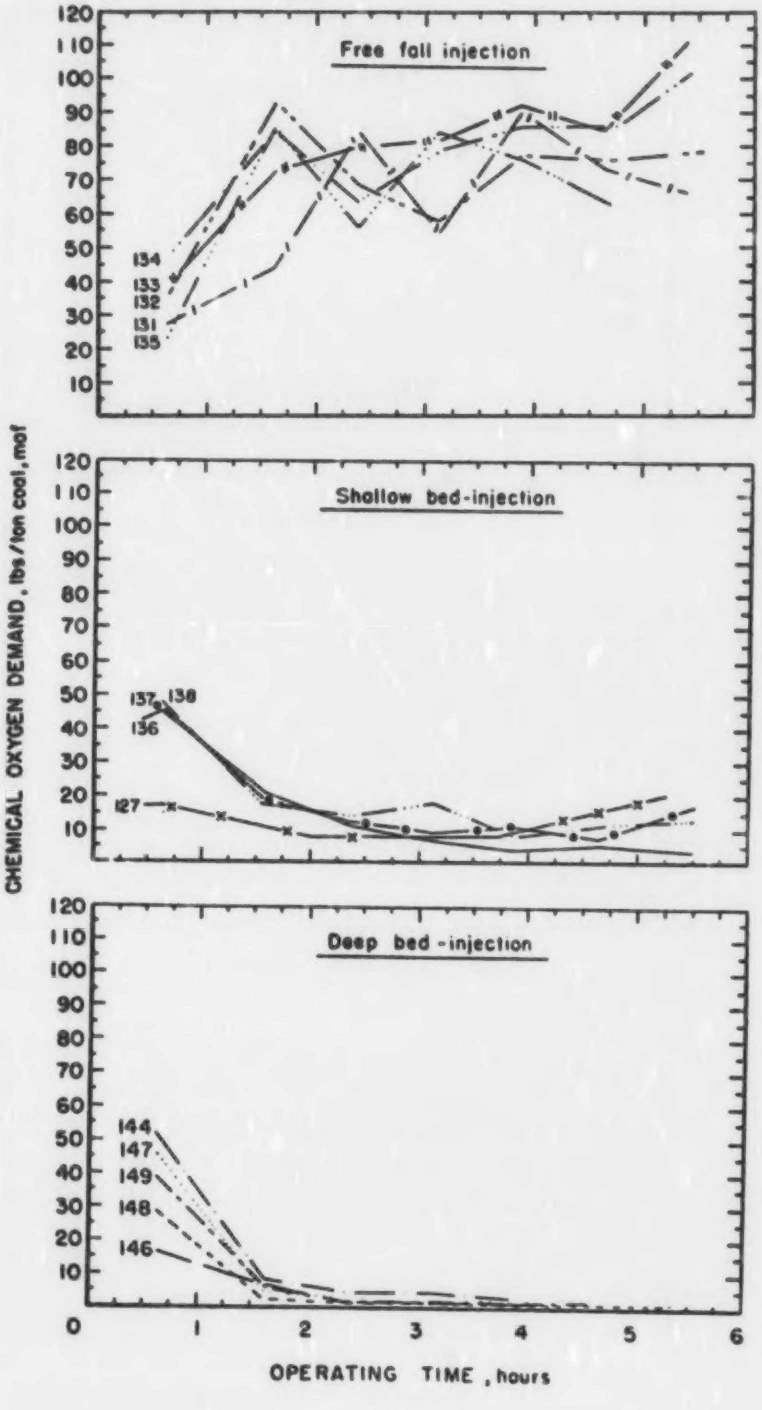


Figure 9. Chemical oxygen demand in byproduct water versus time: gasification of North Dakota lignite.

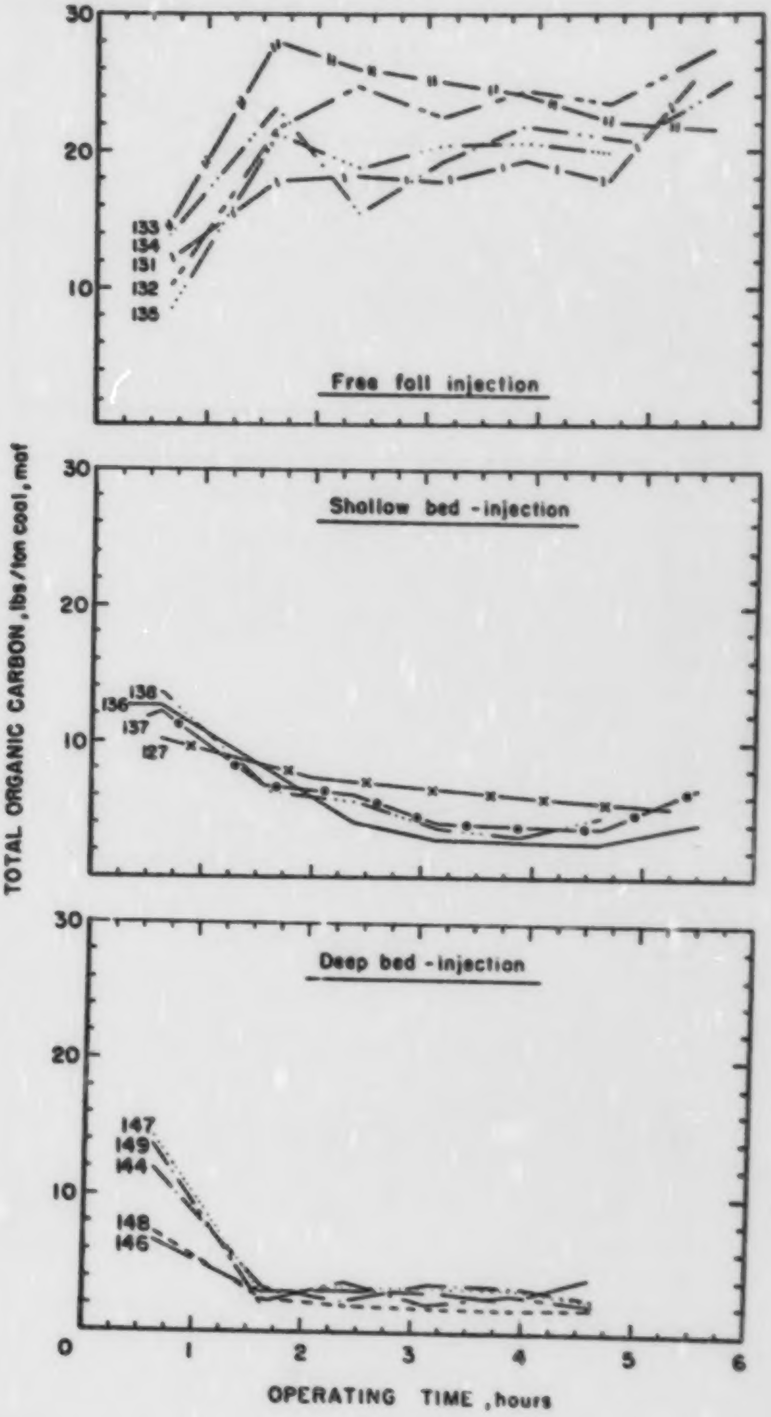


Figure 10. Total organic carbon in byproduct water versus time: gasification of North Dakota lignite.

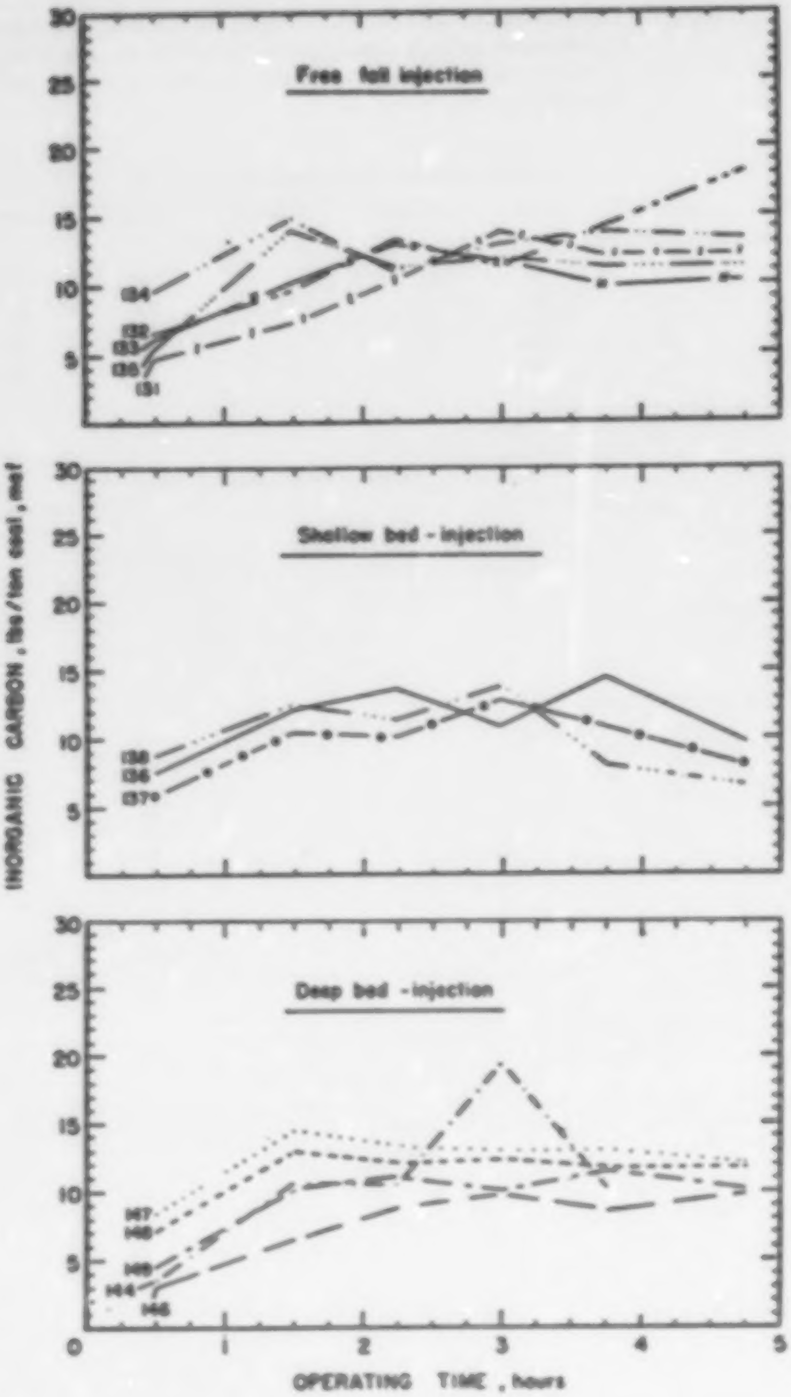


Figure 11. Inorganic carbon in byproduct water versus time: gasification of North Dakota lignite.

Table 2. Time series measurements: thiocyanate content of aqueous condensates collected during the steam-oxygen gasification of North Dakota lignite: free-fall, shallow, and deep bed-injections

	Aqueous Thiocyanate Concentrations, ppm						
Trial	**1-1/4 hrs**	**2 hrs**	**2-3/4 hrs**	**3-1/2 hrs**	**4-1/4 hrs**	**5 hrs**	**5-3/4 hrs**
Free Fall Injection Tests							
CRFFL-131	13	16	13	12	18	7	13
CRFFL-132	<5	<5	<5	<5	<5	<5	<5
CRFFL-133	11	9	12	11	11	7	7
CRFFL-134	20	18	20	21	20	20	18
CRFFL-135	25	25	30	24	23	13	4
Shallow Bed-Injection Tests							
CRFFL-127	←						→
CRFFL-136				Values consistently <5 ppm			
CRFFL-137							
CRFFL-138	←						→

	Trap #1[(a)]	Trap #2[(a)]	Trap #3[(a)]
CRFFL-123	<5	<5	12
CRFFL-124	<5	<5	7
CRFFL-125	<5	<5	<5
CRFFL-126	<5	--	--

Deep Bed-Injection Tests	1-1/4 hrs	2 hrs	2-3/4 hrs	3-1/2 hrs	4-1/4 hrs	5 hrs	5-3/4 hrs
CRFFL-143	17	↖		↗	7	↑	3
CRFFL-144	↑				↑		↑
CRFFL-146							
CRFFL-147	<5		consistently <5 ppm		<5	<5	<5
CRFFL-148	↓	↙		↘	↓	↓	↓
CRFFL-149							

Notes

(a) Batch sampling of condensate was carried out for four experiments. In these cases,
- Trap #1 contains condensate collected in condenser #1 (Figure 1) over the course of the entire run.
- Trap #2 contains overflow condensate from condenser #1.
- Trap #3 contains condensate collected in condenser #2 (Figure 1) over the course of the entire run.

Note that significant concentrations of thiocyanate are detectable only in Trap #3. This is consistent with the fact that water was condensed at a lower temperature in condenser #2.

Table 3. Phenol compound distribution in typical synthane PDU gasifier condensates as a function of coal injection geometry

Compound Present in Condensate	Free Fall Injections, ppm		Shallow Bed-Injections, ppm		
	CHPFI-49	CHPFI-55	CHPFI-80	CHPFI-96	CHPFI-97
Phenol	3,400	2,660	1,300	1,270	1,000
Cresols	2,840	2,610	530	890	930
C_2-phenols	1,090	780	140	270	330
C_3-phenols	110	100	20	50	50
Dihydrics	250	540	60	20	20
Benzofuranols	70	100	30	40	50
Indanols Acetophenones	150	100	40	50	60

Table 4. Summary statistics on char and tar production as a function of coal injection geometry

Item	Free Fall Injection	Deep Bed-Injection	Deep Bed-Injection
Char Yield, lbs/ton coal, MAF	418 ± 77	510 ± 55	729 ± 75
Ultimate Analysis, wt %			
C	52.4 ± 4.8	61.3 ± 8.7	64.8 ± 3.3
H	1.2 ± 0.2	1.3 ± 0.1	1.8 ± 0.5
S	0.3 ± 0.1	0.3 ± 0.1	0.8 ± 0.2
O	3.9 ± 0.8	3.8 ± 0.7	5.5 ± 1.9
N	0.5 ± 0.1	0.4 ± 0.0	0.6 ± 0.1
Ash	41.9 ± 5.3	32.4 ± 9.0	27.5 ± 6.3
Estimated HHV, BTU/lb . .	8135 ± 796	9513 ± 1344	10,216 ± 628
Combustion Equivalent lbs SO_2/MMBTU	0.74 ± 0.27	0.72 ± 0.18	1.47 ± 0.43

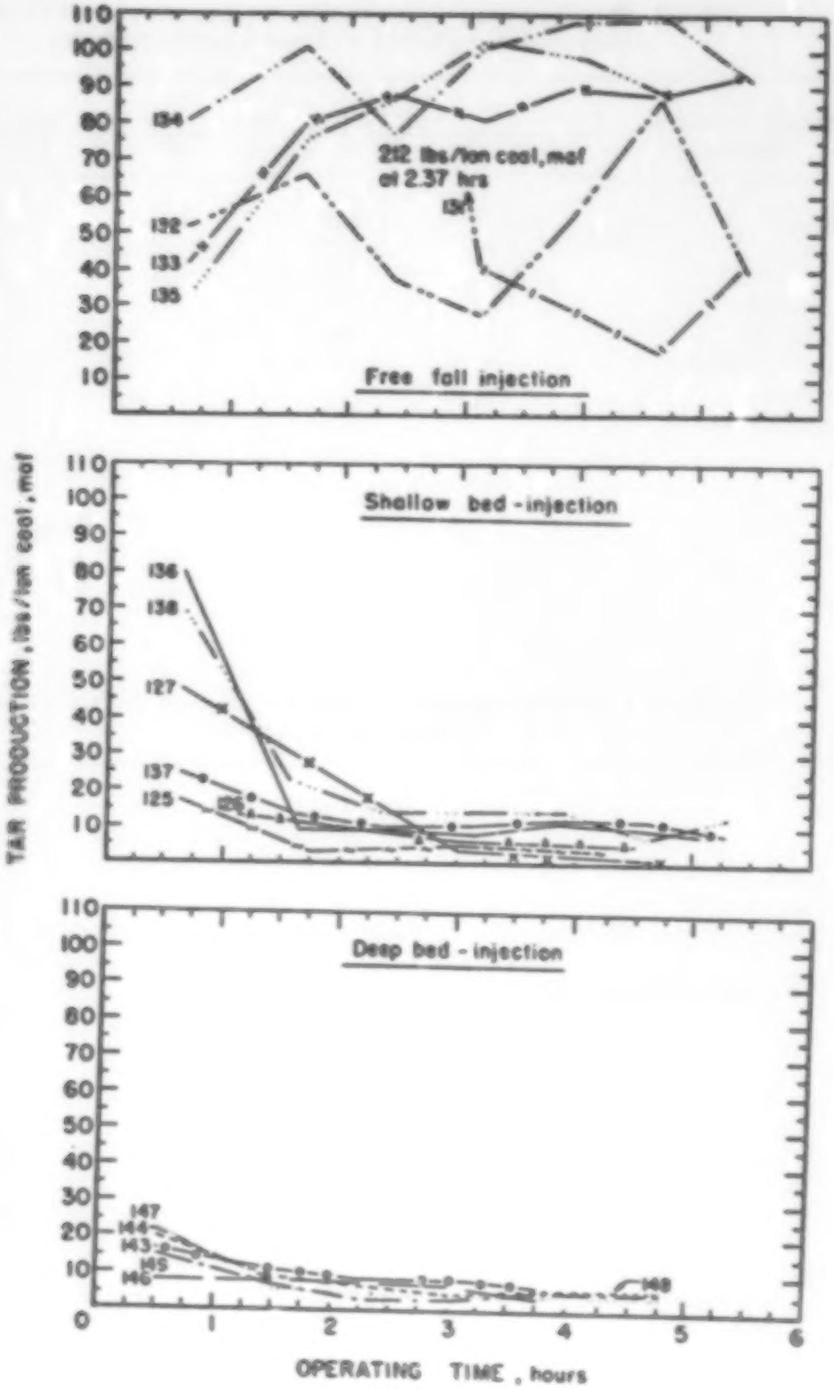


Figure 12. Tar production versus time: gasification in North Dakota lignite.

Table 5. Sulfur content as a function of time, free-fall injection of coal into the synthane PDU gasifier

Trial	Sample Time, hrs	wt % S in Tar	Equivalent lbs SO_2/MMBTU
131	0.63	1.25	1.87
	4.63	0.82	1.14
133	2.38	0.90	1.17
	4.13	0.79	1.05
135	0.63	0.98	1.44
	3.88	0.83	1.11

steady state tar production levels range from a high of ~100 lbs/ton coal, MAF (free-fall injections) to a low of ~5 lbs/ton coal, MAF (deep bed-injections). In contrast to previously reported batch data on tar production during gasification (ref. 2), present time series data—particularly those for shallow and deep bed-injection tests, are highly reproducible from run to run.

Tar Composition

Ultimate analyses (including sulfur content), estimated high heating values (BTU/lb), and approximate sulfur combustion emission rates (equivalent lbs SO_2/MMBTU) were determined for a limited number of tar samples collected at different times during several gasification tests. Tar sulfur contents consistently exceeded the Federal New Source Performance Standard for liquid fuels of 0.8 lbs SO_2/MMBTU (ref. 5). However, as is apparent from the free-fall time series data on tar sulfur shown in table 5, tar composition approaches steady state only slowly, with sulfur content declining steadily from initially high levels. While a similar trend is expected for shallow and deep bed-injection tars, data have not been gathered to confirm this. A major reason for this is a lack of sufficient sample to conduct a reliable analysis. As indicated earlier, tar production rates fall precipitously as coal is injected deeper into the gasifier.

Tar/water emulsions initially complicated efforts to determine densities and true boiling point (TBP) curves for selected hydrocarbon samples. A satisfactory distillation procedure eventually was developed for the dehydration of tar samples. Subsequent analyses of dehydrated samples indicate densities consistently greater than 1.0.

TBP distillation curves for a limited number of dehydrated tar samples are presented in figure 13.[*] Note first that regardless of coal injection geometry, the initial boiling point of each of the samples analyzed is substantially in excess of 100° C. This suggests the presence of essentially no low molecular weight hydrocarbons, in particular benzene, toluene and xylene (BTX). Secondly, note that depending upon the sample considered, from 30 to 60 percent of the hydrocarbons present in the tar boil at temperatures in excess of 500° C. No trend in TBP curves with coal injection geometry is discernible from the limited data available in figure 13. Curves for two shallow bed-injection samples (138A and 138D) lie above the curves for the free-fall injection samples (131D and 132D), and two (137A and 137B&C) lie below; the curve for the one available deep bed-injection sample lies below that of the free-fall sample. A trend in the shape of TBP curves with reactor operating time is suggested for individual gasification runs. Tars collected late in a gasification run (samples 137B&C and 138D) have higher TBP curves, i.e., contain a slightly larger fraction of lower molecular weight hydrocarbons, than tars collected early in a run (samples 137A and 138A). However, interestingly, observed shifts toward lower molecular weight tars do not give rise to increases in BTX production, at least as measured by their presence as constituents in the tar. The BTX content of the product gas was not monitored.

---

[*] Inherently low tar production rates in shallow and deep bed-injection tests limited the extent of meaningful sampling and analysis. In the specific case of deep bed-injection tests, only one sample collected was large enough to yield a workable quantity of tar following dehydration.

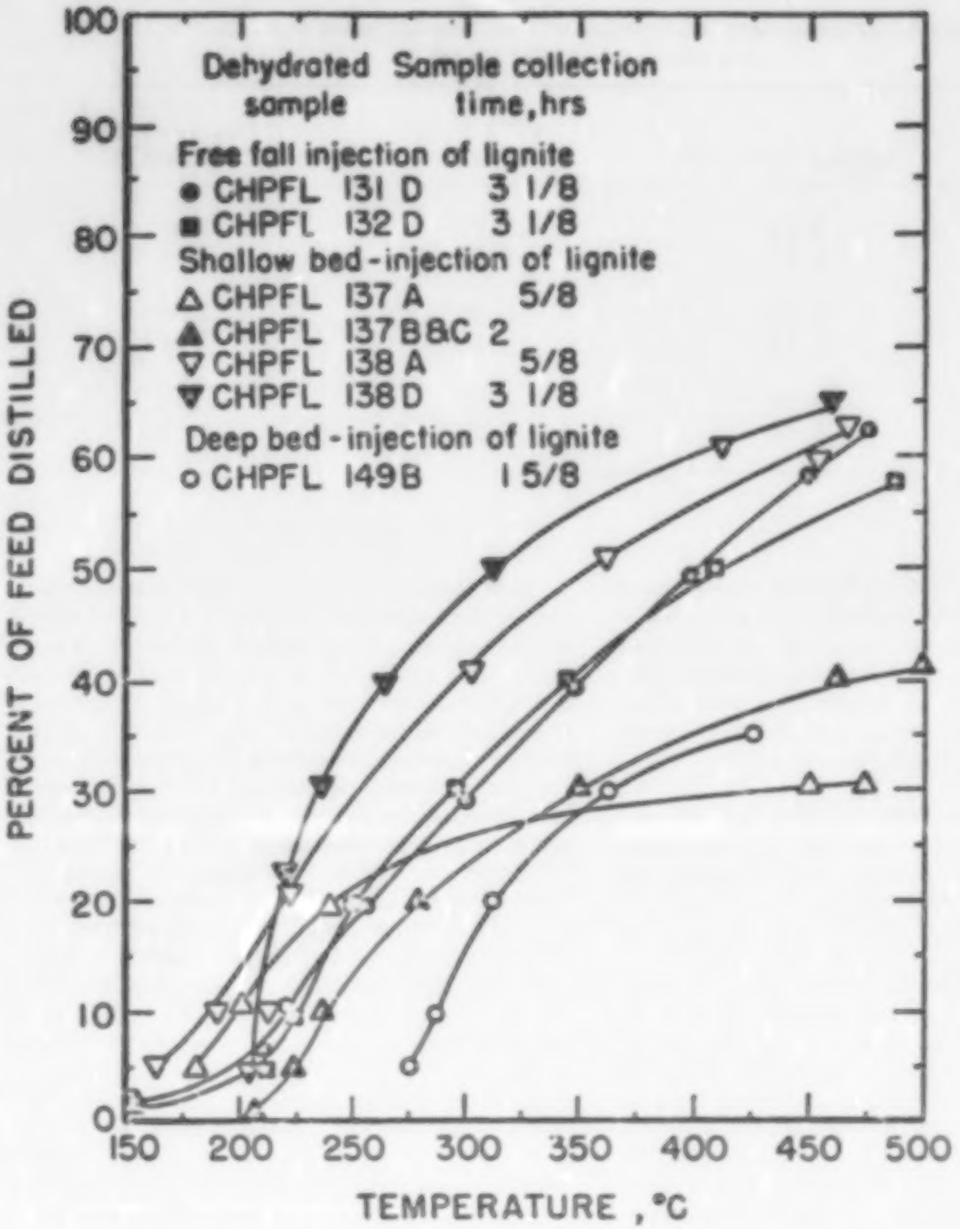


Figure 13. True boiling point determinations of tars produced during the gasification of North Dakota lignite: free-fall, shallow, and deep bed-injections of the coal.

DISCUSSION OF RESULTS

Time Series Analyses of Effluent Production and Composition

As had been expected, individual effluent production rates were found to vary significantly with time from reactor startup to shutdown. Available data indicate that individual production rates are typically high during reactor startup, and decline with time, typically approaching steady state levels after about 2 to 3 hours of reactor operation. Unexpectedly, effluent production rates in the free-fall injection trials ran counter to this trend; production rates consistently increased with time following reactor startup. However, regardless of the coal injection geometry involved, it is significant to note that, for a given mode of gasifier operation, effluent production rates are consistently reproducible, a result not achieved previously where batch sampling techniques were employed for effluent collection (ref. 2).

Interestingly, certain effluent compositions as well as production rates vary significantly with time. For example, the sulfur content of tar declines substantially during the first 3 to 5 hours of gasifier operation. Although not monitored in this experimental program, the composition of char, in particular its sulfur content, is expected to vary similarly with time.

On the basis of the extensive time series analyses presented here, it is evident that not only steady state production rates but, in certain cases, the composition of individual effluents must be known to assess accurately the types and sizes of process equipment needed for satisfactory effluent treatment. Effluent data obtained from the analysis of batch samples collected over an entire run, e.g., past PERC batch data (refs. 1,2), while qualitatively helpful in characterizing the effluent potential of a particular coal or reactor operating procedure, are not sufficiently precise to form a basis for the detailed design of an effluent treatment system.

Effect of Coal Injection Geometry on Gasifier Steady State Effluent Production and Composition

(1) Effluent Production Rates

The 19 tests conducted in this experimental program amply demonstrate that gasifier operating practice, specifically the coal injection position within the gasifier, strongly influences steady state rates of production of the full range of reactor effluents. A statistical summary of steady state values of the 7 indicators of effluent production monitored throughout this study is presented in table 6. For purposes of comparison, similar data also are presented (where available) for weak ammonia liquor typical of a steel industry coke plant effluent. Note first that phenol production rates and chemical oxygen demand (COD) are more than a factor of 10 greater for the free-fall gasification of lignite than for the manufacture of blast furnace coke. However, cyanide and thiocyanate production are more than a factor of 10 lower. Secondly, note that, although dramatic reductions in gasifier effluent production are achieved by shifting from free-fall to deep bed-injection of lignite, residual phenol and COD levels are still roughly equivalent to those of untreated coke plant weak ammonia liquor. Tar production levels are greatly reduced from free-fall to deep bed-injection tests—by more than a factor of 10. However, notice that the largest percentage reduction in gasifier tar production, viz., 86.4 percent, resulted from the shift from free-fall to shallow bed-injections of lignite. Increasing the depth of injection of lignite from 1-½ to 4-½ ft in the fluidized bed portion of the gasifier (deep bed-injections) resulted in an additional reduction of only 37.6 percent. Similar trends in chemical oxygen demand (COD) and total organic carbon (TOC) of aqueous effluents are apparent; COD's are reduced by 84.2 and 69.5 percent, TOC's by 78.2 and 43.8 percent, respectively. Interestingly, the above pattern does not hold for phenol production. Shifting from free-fall to shallow bed-injections of lignite results in a 70.4 percent reduction in phenol production; however, shifting from shallow to deep bed-injections of lignite results in a further reduction in phenol production of 85.7 percent. Such evidence strongly suggests that different mechanisms may be responsible for observed reductions in various steady state effluent production rates with changes in fresh coal injection geometry.

On the basis of data presented here, it appears that with additional residence time, *i.e.*, injection of coal into a deeper fluidized bed, and/or increased reaction temperature, essentially zero rates of production of the major effluents—tar, phenol, and COD—could be achieved. Conoco Coal Development Company (ref. 9) experience with its CO_2-acceptor pilot plant in Rapid City, South Dakota, tends to support this supposition. There, essentially no hydrocarbons heavier than methane are detected in gas leaving a fluid bed reactor operated at 1400-1500° F with a gas residence time of about 20 seconds.

(2) Tar Composition

Although tar production rates drop precipitously with the shift from free-fall to deep bed-injection of lignite, the overall composition of condensible hydrocarbons remains remarkably similar (see true boiling point curves in figure 13). This is an unexpected result. It has been presumed that reductions in the yield of heavy tar would be paralleled by a greatly increased production of light hydrocarbons including benzene, toluene, and xylene (BTX). In fact, little, if any BTX

Table 6. Comparative steady state effluent production rates: byproduct coking, free-fall, shallow, and deep bed-injections of North Dakota lignite

Pollutant	Byproduct Coke Plant[(a)]	Gasification of North Dakota Lignite Free-fall Injection	Shallow Bed-Injection	Deep Bed-Injection
Tar, lbs/ton coal, MAF	93	74.1 ± 27	10.1 ± 5	6.3 ± 2.2
Phenol, lbs/ton coal, MAF	0.86 - 0.97	11.9 ± 1.3	3.5 ± 1.9	0.5 ± 0.6
Chemical Oxygen Demand, lbs/ton coal, MAF	4.0 - 5.5	77.7 ± 14.4	11.8 ± 5.4	3.6 ± 2.4
Total Organic Carbon, lbs/ton coal, MAF	1.60 - 1.96	22.0 ± 3.3	4.8 ± 1.3	2.7 ± 0.7
Inorganic Carbon,[(c)] lbs/ton coal, MAF	N.D.	12.5 ± 2.4	11.0 ± 2.3	11.4 ± 2.4
Cyanide, lbs/ton coal, MAF	0.018 - 0.054	Negligible	Negligible	Negligible
Thiocyanate, lbs/ton coal, MAF	0.31 - 0.35	0.045 ± 0.083	≤0.016 ± 0.002[(b)]	≤0.017 ± 004 [(b)]

Notes
(a) Sources: References 4, 6, 7, and 8.
(b) Measurements at or below the limiting sensitivity of the analytical method employed.
(c) The relatively constant inorganic carbon production levels reported for different lignite injection positions are expected and reflect the presence of a saturated amount of CO_2 in basic (pH of 9) condensate.

was found in free-fall tars, and no significant percentage increase in light hydrocarbons was observed as overall tar production declined. This observation may be important in view of various independent reports of high yields of BTX in bench-scale experiments in which coal is heated rapidly, exposed to high partial pressures of hydrogen for a short time (typically less than 10 sec), and subsequently quenched (refs. 10,12). While coal heatup rates were necessarily relatively low in all the free-fall injection tests (most of the length of the carbonizer was heated to only about 400° C; see figure 3), they were quite rapid in both the shallow and the deep bed-injection tests. At the same time, gas residence times at the elevated temperatures in the fluid bed portion of the gasifier were relatively short, less than 7 seconds even in the deep bed-injection tests. The essentially complete lack of BTX production (i.e., condensed BTX; quenched product gas was not analyzed for BTX) under these conditions as well as the consistently high molecular weight of residual tar stand in sharp contrast to smaller-scale laboratory results referenced above. While hydrogen partial pressures were significantly lower in the present experiments (approximately 180 versus 1000 psig or more) and there was a significant partial pressure of water in each of the present tests, the relevance of these differences is unknown.

Effect of Coal Injection Geometry on Total Product and Methane Gas Yields

Summary statistics on gasifier temperature profiles, total product gas, equivalent methane yields, and effective product gas residence times for each of the three coal injection geometries investigated in the current program are presented in table 7. Within the accuracy of the data available and on the chosen basis of SCF/lb of carbon gasified, equivalent methane yields are essentially unaffected by changes in coal injection geometry. Total product gas production rates are similarly unaffected. However, as indicated by the increasing carbon content of residual char with increasing depth of coal injection, apparently stable gas makes on a SCF/lb of carbon gasified may be deceiving. The efficiency of char gasification generally declines rapidly with carbon content, suggesting that at equal percentage carbon conversions for free-fall, shallow, and deep bed-injections of coal methane and total product gas production rates may differ. Additional experiments are needed to determine whether or not methane and/or product gas yields are influenced by coal injection geometry and, if so, how much.

Possible Mechanisms to Explain Observed Results

It is startling to find that production rates of essentially all undesirable "byproducts" of coal gasification (except sulfur) can be dramatically reduced by minor modifications in gasifier design with apparently negligible reduction in desirable products, viz., equivalent methane, total product gas and ammonia. Such a result clearly suggests that distinctly different mechanisms must be at work in the production and/or destruction of various gasifier constituents. In varying the coal injection geometry from free-fall to deep bed-injection, several operating conditions change in the gasifier. Among these are: (1) the heatup rate of the fresh coal is greatly increased; (2) the mean reaction temperature is increased; (3) gas-solid mixing is enhanced; (4) product gas residence time is increased; and (5) contact between fresh product gas and potentially catalytic char particles is increased. Depending upon the specific coal injection geometry involved, changes in various subsets of these operating conditions tend to dominate.

In shifting from free-fall to shallow bed-injections of coal, the major reactor conditions undergoing change are fresh coal heatup rate and mean reaction gas temperature. Although a study is needed to verify it, a major portion of the observed improvement in effluent production might well be attributed to a reduced rate of formation under the more severe conditions of shallow bed-injection operation rather than to decomposition of formed material. However, even if such a supposition is shown to be correct, it cannot account for all of the observed reduction in effluent production rates since deep bed-injections of lignite produce additional reductions in effluent production. Further, since reaction temperatures in the deep bed-injection tests were actually lower than those in the shallow bed-injection tests, temperature cannot explain the observed reductions. The only significant changes in operating conditions appear to have been increased product gas residence time and additional gas-solid contacting. It would appear that at least these two significant mechanisms influence observed reductions in effluent production with shifts from the shallow to the deep bed coal injection geometry. No attempt was made in the present experimental program to sort out the dominant mechanisms involved. However, bench-scale work is now in progress to determine the relative importance of various reactor operating parameters in effluent production.

Applicability of Current Results to Other Coals and/or Different Gasifiers

Lignite coal was selected for testing here specifically because it is a noncaking coal. Although caking coals (e.g., Illinois No. 6 and Pittsburgh Seam) appear to produce most effluents in yields similar to those of lignite (see data available in reference 2), they differ in one important respect: tar production is substantially greater for caking than for noncaking coals. In addition, due to their agglomerating properties during heatup, caking

Table 7. Summary statistics, gasification of North Dakota lignite: free-fall, shallow, and deep bed-injection of the coal

Parameter	Coal Feed Configuration[a] Free Fall Injection	Coal Feed Configuration[a] Shallow Bed-Injection	Coal Feed Configuration[a] Deep Bed-Injection
Fluid Bed Temp Profile, °C			
Bottom	866 ± 9.00 (5)	843 ± 26.00 (8)	803 ± 20.00
Average	828 ± 5.00 (5)	789 ± 8.00 (8)	773 ± 12.00 (6)
Top	768 ± 36.00 (5)	723 ± 13.00 (8)	723 ± 10.00 (6)
Total Product Gas			
SCF/lb C Gasified[b,c]	33.26 ± 2.10 (4)[f]	29.76 ± 3.10 (8)	35.50 ± 2.30 (5)[g]
Equiv. CH_4 Production			
SCF/lb C Gasified[b,d]	5.70 ± .47 (4)[f]	5.92 ± 1.13 (8)	5.62 ± 0.47 (5)[g]
Effective Gas Residence			
Time, sec[e]	-0-	2.82 ± .11 (8)	6.62 ± .11 (6)

(a) Data in parentheses throughout this table indicate the number of experiments considered in reported average results.

(b) Gas production figures are stated relative to lbs of carbon gasified for wide variations in the extent of gasification achieved.

(c) Total gas production includes CH_4, C_2H_6, H_2, and CO.

(d) Equivalent CH_4 is the sum of SCF of CH_4 and twice the SCF of C_2H_6.

(e) Estimated effective residence time of freshly volatilized coal hydrocarbons in the high temperature, fluidized bed portion of the gasification reactor (see Figure 2). Calculations are based on an assumed plug flow of gases through the reactor. The effective residence time for all free fall runs is assumed to be essentially zero.

(f) Run CHPFL-133 has been omitted from this average.

(g) Run CHPFL-143 has been omitted from this average.

coals are difficult to feed to a gasifier in any geometry other than free-fall. PERC efforts to date to inject pretreated caking coal directly into the fluidized bed portion of the Synthane gasifier have been unsuccessful. If a satisfactory means of injection is eventually found, results of the present study on lignite indicate that more severe processing conditions will be required to treat caking coal to reach the reduced levels of effluent production achieved with lignite.

Without some quantitative understanding of the mechanisms responsible for the reductions in effluent production observed here, projections of possible effects in other gasifiers are speculative at best. A qualitative interpretation of the data here suggests that observed effluent reductions are not specific to the Synthane gasifier; this should be achievable in other reactors.

REFERENCES

1. Albert J. Forney et al., "Analyses of Tars, Chars, Gases, and Water Found in Effluents from the Synthane Process," Bureau of Mines Technical Progress Report No. 76, U.S. Department of the Interior, January 1974.
2. D. V. Nakles, M. J. Massey, A. J. Forney, and W. P. Haynes, "Influence of Synthane Gasifier Conditions on Effluent and Product Gas Production," PERC/RI-75/6, Energy Research and Development Administration, December 1975.
3. C. E. Schmidt, A. G. Sharkey, and R. A. Friedel, "Mass Spectrometric Analysis of Product Water from Coal Gasification," Bureau of Mines Technical Progress Report No. 86, U.S. Department of the Interior, December 1974.
4. H. H. Lowry, editor, *Chemistry of Coal Utilization Volumes I and II*, John Wiley & Sons: New York, 1945.
5. "Standards of Performance for New Stationary Sources," *Federal Register* 36 (247), pp. 24876-24895.
6. P. J. Wilson, and J. H. Welles, *Coal, Coke and Coal Chemicals*, McGraw Hill: New York, 1950.
7. R. D. Hetner, G. R. Tallon, and C. W. Fischer, "Coke Plant Effluent Treatment Investigations," Presentation at the Eastern States Blast-Furnace and Coke Association Winter Meeting, Pittsburgh, Pa., February 12-13, 1970.
8. R. W. Dunlap and F. C. McMichael, "Environmental Impact of the Treatment and Disposal of Coke Plant Wastewaters," Environmental Studies Institute Report, Carnegie-Mellon University, January 17, 1975.
9. Carl Fink, George Curran, and John Sudbury, "CO_2 Acceptor Process Pilot Plant - 1975, Rapid City, South Dakota," Presentation at the Seventh Synthetic Pipeline Gas Symposium, Chicago, Illinois, October 27, 1975.
10. "Improved Techniques for Gasifying Coal," Second Annual Briefing of the Clean Fuels Institute, Department of Chemical Engineering, The City College of New York, January 13-14, 1975.
11. Meyer Steinberg and Peter Fallon, "Coal Liquefaction by Rapid Gas Phase Hydrogenation," Presentation at the 169th National American Chemical Society Meeting, Philadelphia, Pa., April 6-11, 1975.
12. F. C. Schora, "A.G.A. Coal Gasification Research," Presentation at the Fifth Synthetic Pipeline Gas Symposium, Chicago, Ill., October 29-31, 1973.

ENVIRONMENTAL ASPECTS OF SYNTHOIL PROCESS FOR CONVERTING COAL TO LIQUID FUELS

Sayeed Akhtar, Sam Friedman, and Paul M. Yavorsky*

Abstract

SYNTHOIL process converts high-sulfur coals to low-sulfur, low-ash liquid fuels. A slurry of coal in recycle oil is reacted with hydrogen in the presence of $Co\text{-}Mo/SiO_2\text{-}Al_2O_3$ *catalyst in a turbulent-flow, packed-bed reactor at 450° C and 2,000-4,000 psi. Thus, coal is converted to liquid hydrocarbons and sulfur is eliminated as* H_2S *gas. The liquids and unreacted solids are separated from the gases and centrifuged to obtain a low-sulfur, low-ash liquid fuel. Primarily designed for the conversion of coal to a utility fuel, the process is easily adaptable to the production of distillate fuels if the economics justify. The results of a study of the environmental aspects of the SYNTHOIL process will be reviewed and a quantitative estimate of the effluents from a 75,000 bbl/day SYNTHOIL plant operating on a high-sulfur coal will be presented.*

INTRODUCTION

Availability of environmentally acceptable utility fuels prepared from U.S. coals will eliminate the need for importing low-sulfur utility fuel oils for industrial use. Consequently, conversion of coal to a low-sulfur utility fuel is a high priority objective of ERDA, and several processes addressed to the objective are currently under development. One such process in an advanced stage of development is the SYNTHOIL process. A bench-scale continuous unit processing 0.5 ton of coal slurry per day has been in operation for over 2 years, and a process development unit of 10 tons of coal per day capacity is under construction. Concurrently, engineering study and laboratory investigation of the environmental problems of the process are also in progress. This presentation is a review of this work.

DESCRIPTION OF THE PROCESS

Figure 1 is a flow diagram of a SYNTHOIL plant processing 1,000 tons of coal per hour. The yield of product oil is 3,100 bbl per hour corresponding to a nominal plant capacity of 75,000 bbl per day. The yield of light oil and C_1-C_5 gases also is shown in the figure.

Hydrogen and a slurry of coal in recycle oil are passed through a turbulent-flow, packed-bed reactor charged with pellets of $Co\text{-}Mo/SiO_2\text{-}Al_2O_3$ catalyst. At 2,000-4,000 psi and 450° C, coal is converted to liquid hydrocarbons and the heteroatoms in coal are eliminated as hydrides. The product stream from the reactor is led to a gas disengager where the liquid and unreacted solids are separated from the gases. The liquid stream is passed through a centrifuge to remove the unreacted solids consisting of mineral matter and unconverted coal substance. The centrifuged liquid is a low-sulfur, low-ash product oil, suitable for use as a utility fuel. A portion of the centrifuged oil is recycled to convey more coal into the plant while the rest of it is available as the net product.

The solids from the centrifuge are pyrolyzed to recover an additional quantity of nonpolluting fuel oil. The residues from the pyrolyzer, consisting mostly of mineral matter and some carbonaceous material, is gasified to produce H_2 for the process. If necessary, some coal also may be gasified to produce sufficient H_2 for process requirement.

The gases from the gas disengager are processed through a purification train to remove ammonia and ammonium salts by water wash, hydrocarbon gases and vapors by oil wash, and acid gases by amine wash. The purified hydrogen is combined with makeup hydrogen and recycled to the reactor. The gas purification is conducted at the plant pressure to minimize the cost of recycling the purified hydrogen.

The yield data in figure 1 refer to the processing of a Kentucky coal at 4,000 psi and 450° C (ref. 1). Analysis of the high-sulfur, high-ash, run-of-mine Kentucky coal is given in table 1.

THE PROCESS EFFLUENTS

The scope of this presentation will be limited to the process effluents only. The environmental aspects of the effluents from ancillary activities, e.g., mining and transportation of coal, generation of steam and power for plant use, and transportation of products, will not be included in this paper.

Coal Preparation

SYNTHOIL process will operate on run-of-mine coal with up to 20 percent ash. Mineral matter , run-

---

*The authors are with the Pittsburgh Energy Research Center, Energy Research and Development Administration, Pittsburgh, Pennsylvania.

Preceding page blank

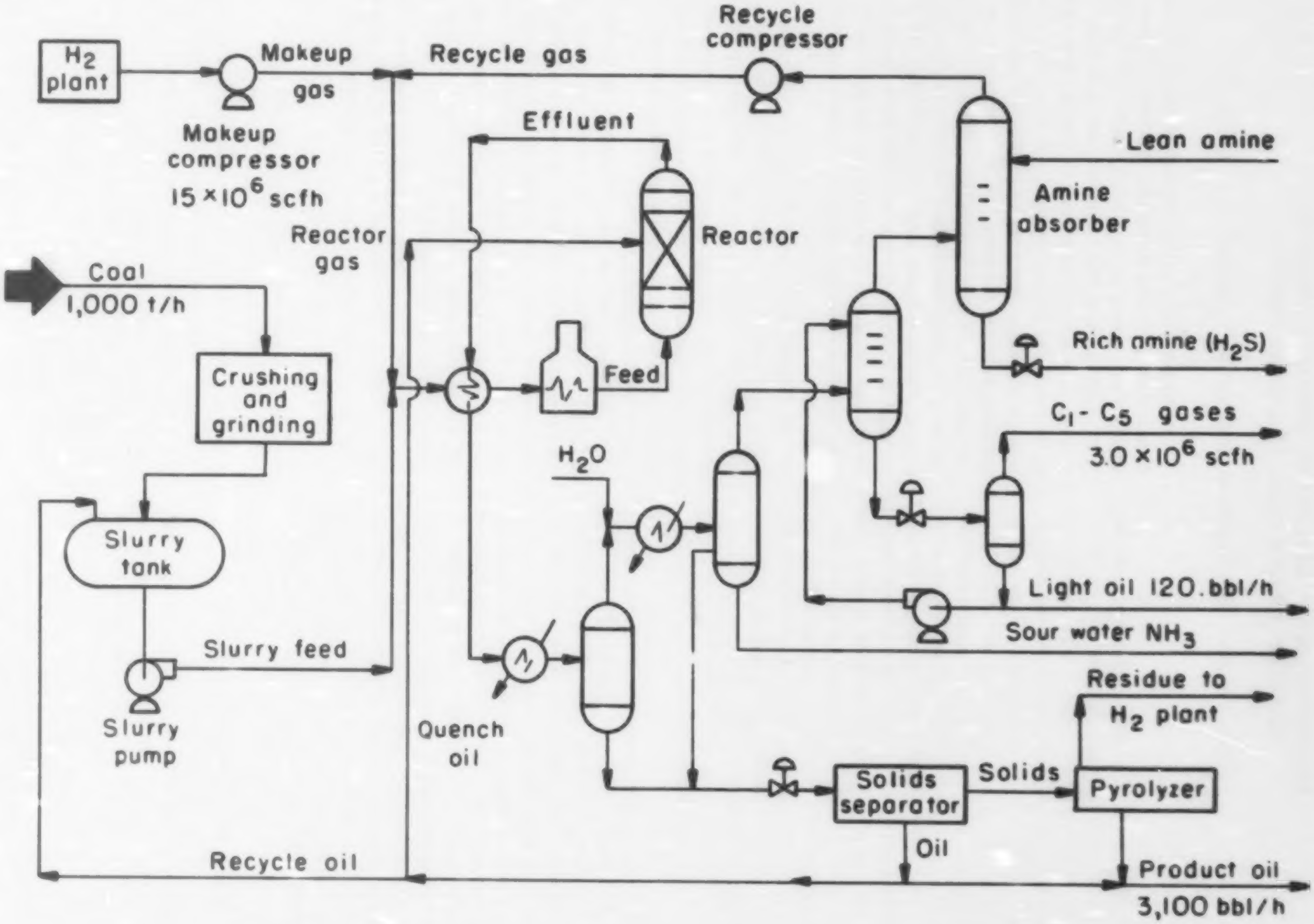

H2 plant
Makeup gas
Makeup compressor
15 × 10^6 scfh
Recycle gas
Recycle compressor
Effluent
Lean amine
Amine absorber
Reactor gas
Reactor
Coal
1,000 t/h
Crushing and grinding
Feed
Rich amine (H2S)
C1 - C5 gases
3.0 × 10^6 scfh
H2O
Slurry tank
Light oil 120 bbl/h
Sour water NH3
Slurry feed
Slurry pump
Quench oil
Residue to H2 plant
Solids separator
Solids
Pyrolyzer
Oil
Recycle oil
Product oil
3,100 bbl/h

Figure 1. Flow diagram for a future commercial SYNTHOIL plant.

Table 1. Analysis of feed coal*, as received

Proximate analysis, wt. %	
Moisture	4.2
Ash	16.5
Volatile matter	36.2
Fixed carbon	43.1
Ultimate analysis, wt. %	
Hydrogen	4.8
Carbon	60.7
Nitrogen	1.2
Oxygen	11.3
Sulfur	5.5
Ash	16.5
Forms of sulfur, wt. %	
Sulfate	0.47
Pyritic	3.08
Organic	1.95
Calorific value, Btu/lb.	11,020
Rank: h.v.A.b.	

*A blend from Kentucky seams 9, 11, 12, and 13 which are mined together; Ohio County, Western Kentucky.

Table 2. Effluents from the coal preparation section of a 1,000 ton coal/hr SYNTHOIL plant

1.	Water evolved in drying coal from an average of 8 pct to 3 pct moisture.	12,500 gph
2.	Dust from crushing, pulverization, and transfer operations.	1 ton/hr
3.	Rain runoff from storage and handling areas.	Indeterminate

of-mine coals, of course, varies with seam and mining method, but currently most eastern coals, after preliminary mine-mouth cleaning to remove mine debris, contain 12 to 20 percent ash. Such coals will be processed without ash reduction. Coal preparation for the SYNTHOIL process will therefore consist of (a) drying to reduce moisture to about 3 percent for efficient pulverization, and (b) comminution to approximately 70 percent through 200 mesh, U.S. standard sieve, and 100 percent through 100 mesh. The effluents from such a coal preparation section will be moisture and dust. A quantitative estimate of these effluents from a 1,000 ton/hr plant is given in table 2. There will also be an indeterminate quantity of rain runoff from the storage and handling area for raw coal. Considerable information on the management of contaminated water from coal mines is now available that will apply to the management of aqueous effluents from the SYNTHOIL coal preparation section (refs. 2,3). The dust can be collected efficiently with baghouse filters and added to the powdered coal.

Slurry Preparation and Pumping

Since the preparation and transfer of coal slurry will be conducted in an enclosed system, the effluent of concern in this section is the vapor leak from pump seals. The concentration of the vapors will, of course, depend on the size of the leak, slurry temperature, and air circulation. An investigation of the air surrounding the slurry preparation and pumping area is currently in progress (ref. 4). The results of this investigation will be presented at a future symposium.

The High-pressure Section

This section comprises the reactor, the heat exchangers, the gas-liquid separator, and the gas purification system. Aside from any accidental release, the effluents of environmental concern from this section will be the following:

1. Sour water, consisting of process make-water and the scrub water injected into the gas stream to dissolve ammonia and ammonium salts.
2. Spent scrub oil from the gaseous hydrocarbon recovery unit.
3. Spent amine solution from the acid gas scrubber.

The contaminants in these effluents will, of course, be determined by the gaseous and entrained impurities in the reactor outlet gas. A mass-spectrometric analysis of the gas is given in table 3. The gas was sampled after the product stream had been cooled and the liquids separated from the gas. The absence of NH_3 from the gas may be noted. Presumably, NH_3 was eliminated quantitatively from the gas phase as solid ammonium sulfide/polysulfide by reaction with H_2S present in excess. Conceivably, other trace components in the gas might also have escaped detection. Nevertheless, they

Table 3. Analysis of SNYTHOIL reactor gas

Component	Volume percent
H_2	94.35
CH_4	2.84
C_2H_6	0.90
C_3H_8	0.61
C_4H_{10}	0.30
C_2H_4	0.03
C_3H_6	0.14
C_4H_8	0.12
H_2S	0.04
CO	0.23
CO_2	0.07
N_2	0.31

will accumulate in the scrub liquids and must be considered while planning disposal of these liquids. We believe substantive research with respect to the scrub liquid effluents will be possible when the 10 ton/day process development unit is operating. The unit will have the gas purification system so that samples of the spent scrub liquids will be available for analysis.

An estimate of the make-water, ammonia, and sulfur from a SYNTHOIL plant processing 1,000 ton/hr of the Kentucky coal is given in table 4.

Solids Separation and Pyrolysis of Solids

As in the slurry preparation and pumping section, the effluent of concern in the solids separation and pyrolysis sections will be organic vapors. The work currently in progress on the investigation of the air surrounding the slurry preparation and pumping area will also be relevant to the problem of organic vapors in the solids separation and pyrolysis sections. A rotary calciner and a fluidized-bed carbonizer are under construction. Quantitative data on effluents from the pyrolysis section will be available when this equipment is in operation.

The carbonaceous residues from the pyrolyzer will be gasified to generate H_2 for the process, and the mineral matter originally present in coal will be ultimately rejected as a solid effluent from the gasifier. This solid will be used as mine fill and, therefore, the extent to which it will contaminate rain runoff is of concern. We plan to study the concentration of leachable salts in solids derived from different coals (ref. 4).

Table 4. Makewater and byproducts from a 1,000 ton coal/hr SYNTHOIL plant

1. Makewater	28,000 gph
2. Ammonia (NH_3)	9 tons/hr
3. Sulfur (S)	38 tons/hr

REFERENCES

1. Sayeed Akhtar, James J. Lacey, Murray Weintraub, Alan A. Reznik, and Paul M. Yavorsky, "The SYNTHOIL Process—Material Balance and Thermal Efficiency," presented at the 67th Annual A.I.Ch.E. Meeting, Washington, D.C., Dec. 1-5, 1974.
2. "Processes, Procedures, and Methods to Control Pollution from Mining Activities," EPA-430/9-73-011, Oct. 1973, U.S. Environmental Protection Agency, Washington, D.C. 20460.
3. Z. V. Kosowski, "Control of Mine Drainage from Coal Mine Mineral Wastes. Phase II: Pollution Abatement and Monitoring," EPA-R2-73-230, May 1973, Environmental Protection Technology Series, Office of Research and Monitoring, U.S. Environmental Protection Agency, Washington, D.C. 20460.
4. Andrew G. Sharkey, Jr., and Coworkers, Pittsburgh Energy Research Center.

ENVIRONMENTAL ASPECTS OF THE SRC PROCESS

Russell E. Perrussel, Walter Hubis, and J. L. Reavis*

Abstract

The prime purpose of the Solvent Refined Coal (SRC) process is to produce a clean, low-ash, low-sulfur solid fuel from high-ash and/or high-sulfur coals of various ranks for use in stationary combustion systems. This paper presents an overview of the SRC process and its associated environmental problems.

Some of the topics discussed are: The process description, plant site, baseline and proposed environmental studies, fugitive particulates and vapors, process waste disposal system, trace elements programs and sulfur plant.

SRC pollution problems are similar to those faced by other industries and can be handled adequately with existing technology to meet environmental standards.

INTRODUCTION

Coal contains inorganic mineral matter and when burned is converted to fly ash, which can go out as particulate matter. Electrostatic precipitators are used to remove most of this fly ash, and a problem exists in removing and disposing of this alkaline fly ash. Coal also contains sulfur compounds, both inorganic and organic. When coal is burned, these sulfur compounds are expelled as oxides of sulfur which are said to be a threat to our ecology. Several methods have been devised to remove these sulfur oxides and fly ash from stack gases. There are different schools of thought as to how successful these removal methods are. Another approach is to remove the mineral matter and sulfur-containing compounds from the coal before it is burned. Several new processes have been developed using this principle. This presentation discusses one such process called the Solvent Refined Coal (SRC) process which is being developed by The Pittsburg & Midway Coal Mining Co. (P&M), under the sponsorship of the U.S. Energy Research & Development Administration (ERDA).

The process provides a solid fuel (which is low in sulfur and ash) to meet environmental requirements, has uniform characteristics regardless of the raw coal processed, and has a high energy content. It is well suited for use as fuel in stationary combustion systems such as used in the electric utility industry for power generation and for a variety of other end uses.

PROCESS OVERVIEW

The Solvent Refined Coal (SRC) process has been described in detail in the literature (refs. 1-6,8) and is very well known. Basically, it is very simple. Figure 1 shows a general block flow diagram of the process with water and gases treatment units. Feed to the preheating section consists of pulverized coal as a slurry in the recycle process solvent where it is contacted with hydrogen. The dissolution step is done at about 850°F and 1500 psig.

The gas phase of the reactor (dissolver) discharge is fed to the acid-gas removal plant where carbon dioxide and hydrogen sulfide are removed by amine scrubbing. The hydrogen sulfide is converted to sulfur in a Stretford sulfur recovery unit. Carbon dioxide is vented to the atmosphere.

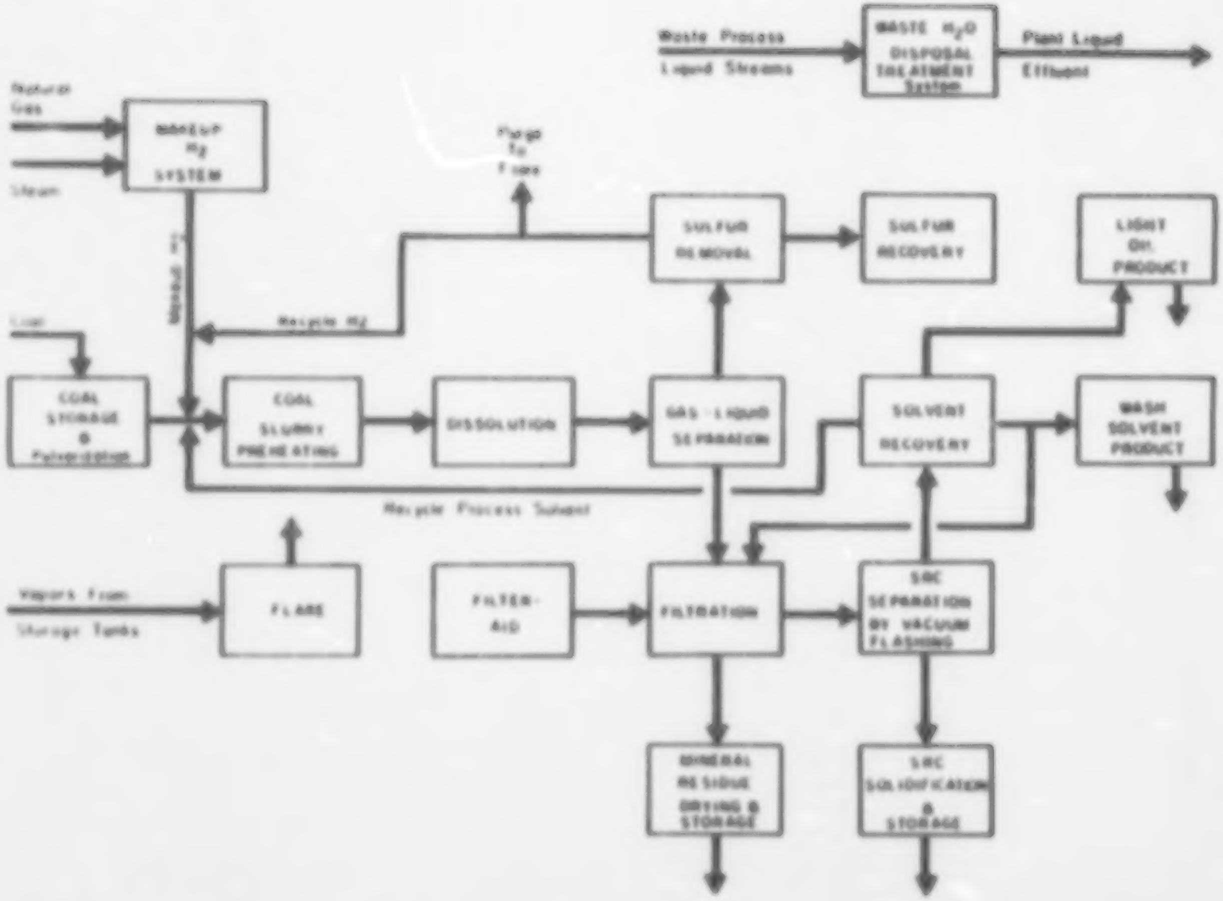
The liquid phase from the gas-liquid separator goes to the filtration area where the insoluble mineral phase is separated using a rotary precoat filter. The filtrate produced in the filtration operation is further separated by vacuum-flashing into a distillate and residue. The distillate is fractionated into a light oil product (coal tar naphtha), wash solvent and recycle process solvent. The residue from the vacuum flashing operation, a low-ash solid with a low-sulfur content, is the major product of the process. This product can be remelted and burned as a liquid fuel or pulverized and burned as a solid fuel. This product will solidify at about 350° F. Whether liquid or solid, it is named Solvent Refined Coal (SRC). The properties and chemical analysis of typical SRC and feed coal (as received and MAF basis) are compared in table 1. The SRC process removes essentially all of the inorganic sulfur, 60-70 percent of the organic sulfur and 98 percent of the ash in the coal. The oxygen is reduced, producing a higher heating value product than the MAF coal.

PLANT SITE

Figure 2 is an aerial photo of the pilot plant located about one mile inside the U.S. Army military reservation at North Fort Lewis (near Dupont), Washington. The plant site covers about 12 acres. Approximately two

---

*R. E. Perrussel is Chief Chemist, The Pittsburg & Midway Coal Mining Co., SRC Pilot Plant, North Fort Lewis (Dupont), WA; W. Hubis is Technical Coordinator, Gulf Mineral Resources Company, Denver, CO; and J. L. Reavis is Project Engineer, The Pittsburg & Midway Coal Mining Co., Research & Development Department, Merriam, KS.



Waste Process
Liquid Streams
WASTE H_2O DISPOSAL TREATMENT System
Plant Liquid
Effluent
Natural Gas
Steam
MAKEUP H_2 SYSTEM
Makeup H_2
Purge To Flare
SULFUR REMOVAL
SULFUR RECOVERY
LIGHT OIL PRODUCT
Recycle H_2
Coal
COAL STORAGE & Pulverization
COAL SLURRY PREHEATING
DISSOLUTION
GAS - LIQUID SEPARATION
SOLVENT RECOVERY
WASH SOLVENT PRODUCT
Recycle Process Solvent
Vapors From
Storage Tanks
FLARE
FILTER-AID
FILTRATION
SRC SEPARATION BY VACUUM FLASHING
MINERAL RESIDUE DRYING & STORAGE
SRC SOLIDIFICATION & STORAGE

Figure 1. Block flow diagram, SRC pilot plant, Fort Lewis, Washington.

Table 1. Comparison of feed coal and solvent refined coal

	Kentucky Coal (Hopkins County)		Typical SRC
	As Received	MAF*	
% Carbon	68.2	78.0	88.0
% Hydrogen	4.8**	5.6	5.9
% Nitrogen	1.3	1.4	2.2
% Sulfur	3.6	1.4*	0.7
% Chlorine	0.05	-	-
% Oxygen (by difference)	8.4**	12.7	3.1
% Moisture	4.8		-
% Ash	8.7		0.2
Forms of Sulfur			
% Sulfate	0.25	-	-
% Pyritic	2.2	-	-
% Organic	1.15	1.4*	0.7
Btu/lb	12,900	14,030	16,250
Fusion point (gradient bar)	-	-	350° F
Density (gm/cc)		-	1.2

---

* MAF or "moisture and ash free: in this case includes only the organic sulfur

**corrected for moisture

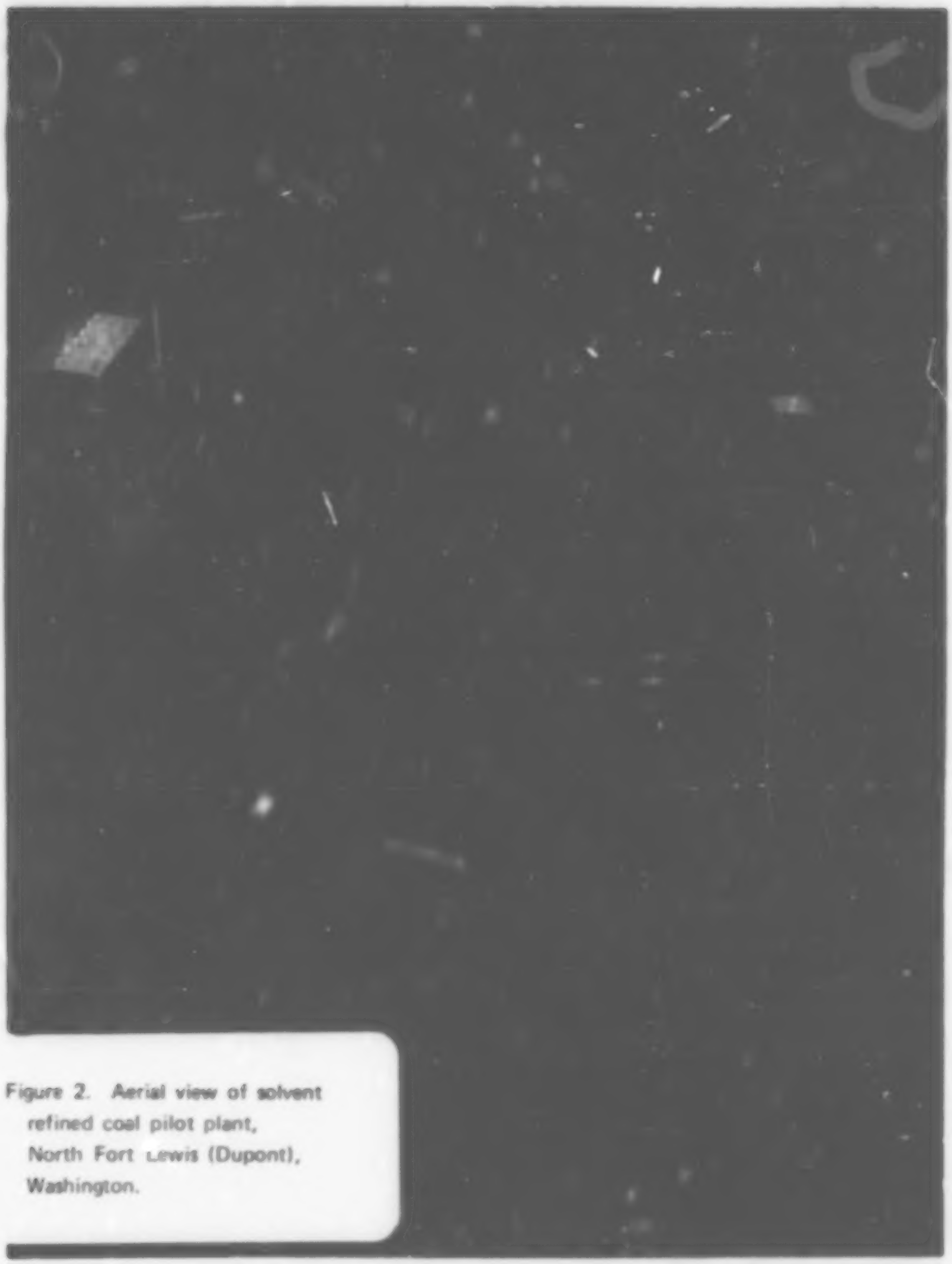


Figure 2. Aerial view of solvent refined coal pilot plant, North Fort Lewis (Dupont), Washington.

years were required for construction at an estimated cost of $20 million. The plant has now been processing coal for over a year with down time being less than 20 percent.

The plant facilities can be conveniently grouped into several areas including coal preparation and handling, coal liquefaction and filtration, gas cleaning and acid-gas removal, product handling and storage, solvent recovery, tank farm, hydrogen production, and finally auxiliary facilities such as steam generation, inert gas manufacture, water treating, and a sulfur plant.

ENVIRONMENTAL CONSIDERATIONS

Any process based on coal will inevitably encounter many environmental problems. In all processes, regardless of nature, all materials coming into its plant site will either become a product for removal or a waste for disposal with their associated pollution problems. The SRC pilot plant is no exception to this.

A large proportion of the total plant cost is devoted to environmentally related matters and to byproduct disposal. The environmental aspects of an SRC plant are similar to those encountered in power plants (coal dust, flue gases), coke plants (coal tar hydrocarbons), and petroleum refineries (distillation, hydrogenation, and handling of solvents, tars and pitches). No unique problems and no greater difficulty in meeting the environmental standards of these industries are anticipated for a commercial SRC plant.

Prior Studies

Some consideration has been given previously to environmental aspects of the SRC liquefaction process in several papers presented at the first EPA symposium on fuel conversion technology. One of these (ref. 5), "Environmental Aspects of SRC Process," was presented about five months before the pilot plant started processing coal.

Exxon Research and Engineering Co. recently completed a report for the EPA (ref. 6). The report gives results of a review of the Solvent Refined Coal (SRC) process of The Pittsburg & Midway Coal Mining Co., from the standpoint of its potential for affecting the environment. It includes estimates of the quantities of solids, liquid, and gaseous effluents, where possible, as well as the thermal efficiency of the process. It proposes a number of possible process modifications or alternatives which could facilitate pollution control or increase thermal efficiency, and points out new technology needs. A complete listing of all plant flow streams and reagents used is reviewed.

In view of the year's operation of the pilot plant, now a more precise definition and discussion of the environmental problems can be presented.

Baseline and Proposed Ambient Air and Water Quality Studies

Before construction on the plant began, an environmental quality assessment was performed in the vicinity of the proposed plant site at North Fort Lewis, Washington (ref. 4). Specifically, an air and water quality study was conducted to establish existing background levels of selected pollutants as a basis for determining any significant environmental changes which may subsequently result from the operation of the new facility.

Overall, the baseline study showed that the air was clean, the water was pure, and the soil—though rocky, would support vegetation consistent to the area.

A new proposal has been drawn up to evaluate the air, water, solid wastes, soils, vegetation, and aquatic biology at the operating plant site and surrounding area. This will be a comprehensive environmental assessment conducted over an extended time. It will include a detailed study of all potential emission sources (flare stack, drier vent, dust collectors, solvent storage tanks, etc.). These data will then be used to design an effective ambient monitoring program.

This facility is one of the first of its kind. An adequate assessment of the environmental problems associated with air and water, and their effects on humans and the vegetation in and near the facility is essential to determine the current environmental impact. This information is necessary to implement process control techniques as well as industrial hygiene safeguards, both at the North Fort Lewis facility and future installations.

Fugitive Particulates and Vapors

Fugitive particulates (dusts) and vapors (fumes) can originate in several areas throughout the plant. Dust problems are imminent when the coal is pulverized, the filter aid precoat slurry is prepared, the mineral residue is dried and discharged, Solvent Refined Coal transferred, or when dry chemical containers are emptied. These are controlled by using covered conveyors and induced draft vents with the vent gas being filtered to remove particulates where possible.

As the coal is pulverized, a hot inert gas dries it and carries it into a bag house. Here the dried, powdered coal is collected for discharge into the slurry blend tank. This operation is in a closed system. The water liberated from the coal is sent to the waste reservoir for treatment.

Diatomaceous earth, with or without asbestos, is used as a filter aid on the rotary filters. In this operation, bags of filter aid are opened, dumped into a hopper for later precoat slurry preparation. To minimize the inhalation of these dusts, a large glove box was designed and constructed. A bag of filter aid is inserted into the box which is then closed. The hands and arms of the operator are then inserted into the "gloves" attached to the box. The bag can then be opened in an enclosed chamber. The box is then placed over the hopper and the released filter aid discharged without evolved dust.

In order to eliminate vapors from the solvent tanks and other vessels, they are enclosed with an inert gas blanket. As this blanket is purged out when a vessel is filled, the gas and vapors are discharged into an inert gas flow. This flow, as well as all of the gases purged from the pilot plant, go into the flare piping system to be carried to the flare stack. All safety relief valves are also connected to the flare system. The gases are burned in the flare stack, supplemented with natural gas if necessary to maintain combustion.

The disposal of mineral residue poses several problems. In a commercial plant, utilization to useful products instead of the costly disposal would make the process more economical. One method is to gasify the mineral residue. A slagging gasifier would convert the mineral residue into a relatively clean slag and synthesis gas (H_2 + CO). The sulfur in the mineral residue would be converted into hydrogen sulfide which would appear in the synthesis gas and could be removed by usual acid gas scrubbing methods. Thus, the slag could be disposed of as land fill. Also, part of the hydrogen needs of the plant would be fulfilled.

Waste Water—Oil Disposal System

Liquid waste streams from the plant are combined and treated in a waste treatment plant consisting of clarification, biological treatment, sand filtration and finally, carbon filtration. A schematic flow diagram of the waste water-oil disposal system is presented in figure 3. No unusual or unexpected problems have been encountered in the operation of this equipment.

The analysis ranges of the water as it goes throughout the treatment units are shown in table 2.

Trace Elements

In assessing all of the pollution aspects of the SRC process, it is necessary to measure and follow the course and fate of trace elements, particularly those of environmental interest.

From previous data (ref. 1), it was shown that the SRC product contains appreciable amounts of certain trace elements, especially titanium, and in many cases these constituents are in different ratios relative to their content in the feed coal. Although titanium is not considered to be one of the more toxic elements, the significance and impact of this element needs to be carefully evaluated.

It is obvious that all trace elements in the coal feed must leave the plant either in the products, or in other gas, liquid, or solid effluents. It is not yet possible to make complete balances due to the early stage of process development.

The Washington State University's Nuclear Radiation Center has contracted to develop a program for the application of neutron activation analysis (both instrumental and chemical) and atomic absorption spectroscopy to the determination of trace elements in the SRC process.

The work to date has been very preliminary. Sampling techniques, sample points and shipping methods have now been worked out. Instrumental neutron activation analyses procedures for all SRC products are now complete. A program has now been set up to do a complete balance on toxic and potentially toxic elements throughout the pilot plant.

In some process designs for coal conversion operations, certain streams are recycled in the process. For the SRC design, this is the case on the sour process water from the liquefaction reactor and process solvent. It will be apparent that if certain trace elements are collected by a recycle stream, they will tend to build up due to recycling since they may not be able to escape. This could apply, for example, to volatile compounds of arsenic, lead, boron, and fluorine. More information is needed to define the problem, and some provision for separating and disposing of trace elements may have to be added.

A review of occurrence and distribution of trace elements in coal is given in ref. 7. Some of the problems encountered in sulfur and nitrogen balances in the Solvent Refined Coal process are discussed in an EPA report (ref. 8).

Sulfur Plant

Some of the sulfur liberated from the coal by processing appears as hydrogen sulfide in various gas streams. The hydrogen sulfide with carbon dioxide is separated by an amine absorption unit. This concentrated gas is sent to a low pressure Stretford Absorber where the hydrogen sulfide is converted to elemental sulfur as a byproduct or waste depending on the local market.

Problems in these conventional units have been limited to those experienced during normal plant startups. In a commercial plant, a Claus sulfur plant would probably be used with an appropriate tail gas cleanup unit. Proven technology with which to build a workable

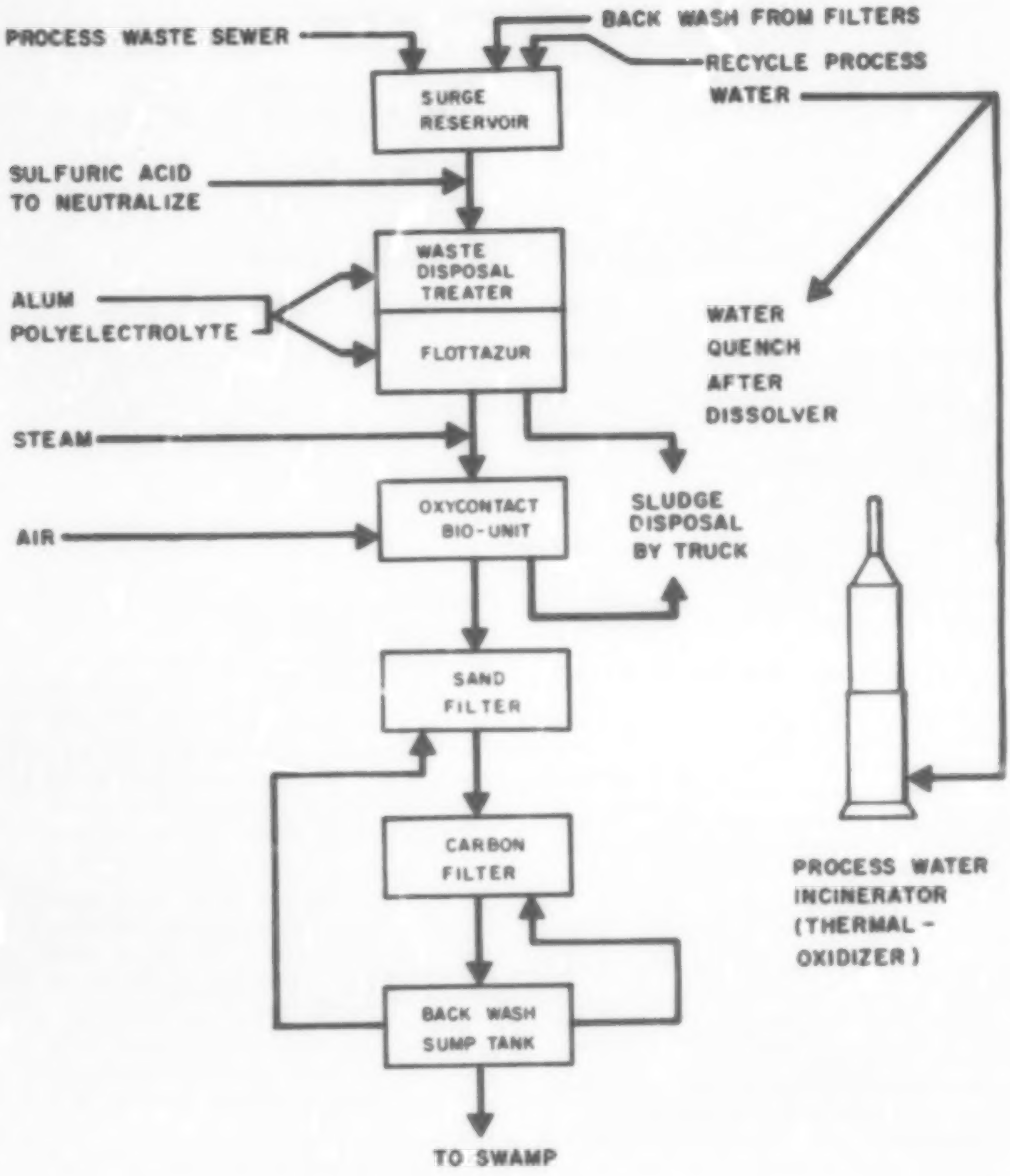

PROCESS WASTE SEWER
BACK WASH FROM FILTERS
RECYCLE PROCESS WATER
SURGE RESERVOIR
SULFURIC ACID TO NEUTRALIZE
WASTE DISPOSAL TREATER
ALUM
POLYELECTROLYTE
FLOTTAZUR
WATER QUENCH AFTER DISSOLVER
STEAM
SLUDGE DISPOSAL BY TRUCK
OXYCONTACT BIO-UNIT
AIR
SAND FILTER
CARBON FILTER
BACK WASH SUMP TANK
PROCESS WATER INCINERATOR (THERMAL - OXIDIZER)
TO SWAMP

Figure 3. Waste water-oil disposal system flow.

Table 2. Average waste treatment analysis ranges

	Surge Reservoir	Waste Disposal Treater	Flottazur	Bio-Unit Effluent	Plant Effluent
pH	6.9-9.0	6.2-6.8	6.2-6.8	6.2-7.4	6.2-7.4
BOD, ppm			135-350	20-110	4-23
COD, ppm	1000-9600	650-5000	500-4000	40-400	5-75
TSS, ppm	90-400	50-300	30-200	20-300	0-20
Phenol, ppm	30-1500	25-1100	10-1000	0.1-3.0	0.0-0.6
Extractable Oil, ppm	10-250	6-150	4-30	0-4	0-3

sulfur recovery plant exists and will be utilized to effectively remove the hydrogen sulfide from the process.

CLOSING REMARKS

Our nation will run out of oil and gas not to long after the year 2000 and we get about three-fourths of our energy from these dwindling sources. Therefore, coal-derived fuels will be needed. The SRC process is another step towards keeping the people of the world from "freezing in the dark" without undue pollution from the utilization of coal.

REFERENCES

1. D. L. Kloepper, T. F. Rogers, C. H. Wright, and W. C. Bull, "Solvent Processing of Coal to Produce a De-Ashed Product," Research and Development Report No. 9, Office of Coal Research, U.S. Department of Interior, 1966.
2. "Development of a Process For Producing An Ashless, Low-Sulfur Fuel From Coal," Research and Development Report No. 53, Interim Report No. 2, Volume III, Part 1, "Design of Pilot Plant," Office of Coal Research, U.S. Department of Interior, 1969.
3. C. H. Wright and D. E. Severson, "Experimental Evidence for Catalyst Activity of Coal Minerals," *PREPRINTS, Division of Fuel, Am. Chem. Soc.*, Vol. 16, No. 2, pp. 88-91 (1972).
4. A. T. Rossano, "Air and Water Quality Assessment Prior to Operation of The Solvent Coal Cleaning Plant," Environment Resources Associates, Inc., Redmond, WA, March 1974.
5. C. R. Hinderliter, "Environmental Aspects of the SRC Process," pp. 159-169, Report EPA-650/1-74-118," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology," Office of Research and Development, U.S. Environmental Protection Agency, October 1974.
6. C. E. Jahnig, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes—Liquefaction: Section 2. SRC Process." Report EPA-650/2-74-009-f, Office of Research and Development, U.S. Environmental Protection Agency, March 1975.
7. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: A Final Report," Illinois State Geological Survey Environmental Geology Note No. 72, 1974.
8. Charles H. Wright, "Sulfur and Nitrogen Balances in the Solvent Refined Coal Process," Report EPA-650/2-75-011, Office of Research and Development, U.S. Environmental Protection Agency, January 1975.

16 December 1975

Session III:

CONTROL TECHNOLOGY

René R. Bertrand, Ph.D.
Session Chairman

LOW AND INTERMEDIATE BTU FUEL GAS CLEANUP

C. B. Colton, M. S. Dandavati, and V. B. May*

Abstract

There is a variety of systems presently available and under development to control the emissions from and protect the turbine of a combined cycle power plant burning fuel gas produced by gasifying coal. In the broadest sense, these processes can be characterized as high and low temperature processes. Many of these processes have unique features governing their application to specific combinations of coal gasifiers and combined cycle power plants. This paper presents an overview of high and low temperature cleanup processes, and addresses the considerations involved in their selection.

INTRODUCTION

For many years, the conventional fossil-fueled steam electric power plant has been the mainstay of the electric utilities. However, faced with oil and natural gas supply problems as well as increasingly stringent environmental regulations, the electric utilities are closely examining their alternatives. One such alternative is the low-Btu gas-fired combined cycle power plant. This type of electric generating facility offers a potential for efficiencies in the neighborhood of 50 percent, as well as for significant reductions in emissions, effluents, solid wastes, and water requirements. While it is true that the efficiency quoted is not obtainable with today's gasifier and combined cycle technology, a concentrated application of engineering resources could make efficiencies in this order of magnitude achievable within the next 10 to 20 years.

With regard to near-term implementation of this low-Btu gasifier and combined cycle technology, it is important to note that there are commercially available gasifiers and low temperature fuel gas cleanup systems. This type of electric power generation facility could be built with today's technology and would probably be competitive with conventional coal-fired power plants. In addition—as was previously mentioned, this type of power plant would offer some significant advantages over conventional coal-fired plants, particularly those firing high sulfur coal.

Both literally and figuratively, the heart of the low-Btu gas-fired combined cycle power plant is the portion of the system that conditions the fuel gas produced by the gasifier prior to its entry and subsequent combustion in the combined cycle turbine. The cleanup system must remove those constituents of the fuel gas that would be harmful to the turbine or that would be harmful to the environment should they be present in a turbine exhaust. In general, the cleanup system serves three functions:

- Fuel gas desulfurization
- Particulate removal
- NO_x control

Some of these systems incorporate processes with principles of operation and design features that only allow them to operate at low temperatures, while others may operate at greatly elevated temperatures. Low temperature systems are arbitrarily defined as those requiring cooling of the dirty fuel gas to 250°F or below, whereas high temperature systems require little or no cooling of the dirty gas as it comes from the gasifier.

LOW TEMPERATURE DESULFURIZATION PROCESSES

Low temperature processes can be subdivided into four categories, according to the principle of operation. These are:

(1) Chemical solvent processes
(2) Physical solvent processes
(3) Direct conversion processes
(4) Dry bed processes

Table 1 lists examples for each low temperature cleanup system category, as well as data for each example process.

Chemical Solvent Processes

These processes employ aqueous solutions of organic and/or inorganic agents to scrub the "dirty" gas. These agents are capable of forming "complexes" with H_2S, CO_2, and other acid gas components present in the raw gas stream. The "complex" is then decomposed during regeneration at elevated temperatures, thereby releasing the acid gases for further processing and recovery. The regenerated solution is recycled for further absorption. These processes may be subdivided into those based on amine scrubbing solutions, and those based on alkali scrubbing solutions. Most of these processes exhibit little or no selective absorption of H_2S over CO_2.

---

*Colton and May are with Hittman Associates, Inc., Columbia, Maryland 21045. Colton is Manager of Advanced Programs; May is a Senior Engineer. Dandavati, previously with Hittman Associates, is now with Gilbert Associates, Reading, Pennsylvania.

Table I. Low temperature cleanup processes

Basis: 3450 ton/day Illinois No. 6 Coal Fed to BCR Gasifier, or 6750 ppm of Influent H_2S

Process	Absorbent	Type of Absorbent	Temp. °F	Pressure	Efficiency of S Removal		Absorbent Characteristics				Form of Sulfur Recovery	Status
					% H_2S Influent	Effluent H_2S ppm	Life	Regeneration	Selectivity toward	Make up rate		
Chemical solvent type												
1. MEA	Monoethanolamine	Aqueous solution	80 to 120	Insensitive to variation in pressure	99	~100		Thermal	Forms non-regen. comp. with COS, CS_2	50 to 100%	As H_2S gas	Commercial
2. DEA	Diethanolamine	Aqueous solution	100 to 120	Insensitive to variation in pressure	99	~100		Thermal	Absorbs CO_2, does not absorb COS, CS_2	< 5%	As H_2S gas	Commercial
3. TEA	Triethanolamine	Aqueous solution	100 to 150	Insensitive to variation in pressure	99	~100		Thermal	H_2S	< 5%	As H_2S gas	Commercial
4. Alkazid	Potassium dimethyl amino acetate	Aqueous solution	70 to 120	Insensitive to variation in pressure 1 - 60 psia	99	~100		With steam	H_2S		As H_2S gas	Commercial
5. Benfield	Activated potassium carbonate solution	Aqueous solution	150 to 250		99	H_2S + COS ~100	Unlimited life [illegible]	With steam	H_2S is high		As H_2S gas	Commercial
6. Catacarb	Activated potassium carbonate solution	Aqueous solution	150 to 250	Insensitive to variation in pressure generally > 250 psi	99	H_2S + COS ~100		With steam	H_2S - partial also absorbs COS, CS_2	< 5%	As H_2S gas	Commercial
Physical solvent type												
7. Sulfinol	Sulfolane + Diisopropanolamine	Organic solvent	60 to 120	High pressure preferred	99	H_2S + COS ~100		Low pressure flashing or with steam	H_2S, and also absorbs COS, CS_2 and mercaptans		As H_2S gas	Commercial
8. Selexol	Polyethylene glycol ether	Organic solvent	20 to 80		99	H_2S + COS ~100			H_2S also absorbs COS		As H_2S gas	Commercial
9. Rectisol	Methanol	Organic solvent	< 0		99	~100			H_2S			Commercial
Direct conversion												
10. Stretford	Na_2CO_3 + anthraquinone disulfonic acid	Alkaline solution			99.9	~10			H_2S	50 to 100%	Elemental sulfur	Commercial
11. Townsend	Triethylene glycol	Aqueous solution	100 to 250		99.9	~10			H_2S		Elemental sulfur	
Dry bed type												
12. Iron sponge	Hydrated Fe_2O_3	Fixed bed	70 to 100		99	H_2S + COS ~100			H_2S and also towards COS, CS_2 and mercaptans		Elemental sulfur	Commercial

Physical Solvent Processes

These processes use organic solvents to remove acid gases by physical absorption, rather than by chemical reaction. The extent of absorption is directly proportional to the partial pressure of the acid gas components. These processes are best-suited to high-pressure gas treating where appreciable quantities of acid gases are present. The solvent is then regenerated by heat and/or pressure reduction, thereby releasing a concentrated stream of acid gases and a recyclable solvent. These processes exhibit a selective absorption of H_2S over CO_2. In addition to removing H_2S and CO_2, these processes are all capable of removing COS, CS_2, and mercaptans without solvent degradation.

Direct Conversion Processes

These consist of two types of processes:

(1) Those based on oxidation reduction reactions; and
(2) Those based on the stoichiometric reaction of H_2S with SO_2 in the presence of a solvent.

In the first type, H_2S is absorbed in an alkaline solution containing oxidizing agents. The H_2S is then oxidized to elemental sulfur by air feeding to the regenerator and the sulfur product is separated from the regenerated solution by froth flotation. Partial removal of COS, CS_2, and mercaptans is also possible.

The second group of direct conversion processes are those in which H_2S is absorbed in a solvent and converted to elemental sulfur by the Claus type reaction with SO_2.

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (1)$$

The solvents are usually aqueous solutions of organic or inorganic agents.

Dry Bed Processes

These are based on absorption of acid gases by a fixed bed of solid absorbent. Due to their low absorbent loading, they are best-suited to removing small quantities of acid gases. These processes can be subdivided into the historical iron oxide processes and the various molecular sieve processes.

Factors Affecting Low Temperature Cleanup System Selection

The following factors emerge as being the most important in selecting low temperature desulfurization systems most appropriate for treating fuel gas:

(1) Sulfur removal capabilities, not only with respect to H_2S, but also other sulfur compounds such as COS and CS_2.
(2) Selective absorption of sulfur compounds over carbon dioxide. The latter need not be removed from low-Btu fuel gas intended for use in advanced power cycles, therefore, its absorption is undesirable since it represents an increased operating load on the cleanup system.
(3) Type of absorbent insofar as the treated fuel gas may contain entrained or volatilized solvent which could be detrimental to downstream system components such as turbine blades, etc.
(4) The system's tolerance to other contaminants present in the raw fuel gas such as ammonia, cyanides, phenols and tars.
(5) Overall energy requirements and operating costs.

HIGH TEMPERATURE DESULFURIZATION PROCESSES

Several high temperature desulfurization processes are currently under development. A list of some of the more noteworthy processes is shown in table 2. None of the processes has been commercialized. However, the Bureau of Mines Sintered Iron-Oxide Process and the Consolidation Coal Company's Half-Calcined Dolomite Process are relatively advanced in their development and may result in commercialization sooner than the others. The principle underlying high temperature desulfurization is the formation of metal sulfides by chemical reaction of the absorbent with sulfur compounds in the gas at high temperatures. The extent of sulfur removal depends on the chemical equilibria for the particular system. The following three high temperature desulfurization processes will be discussed in this presentation since they are generally representative of various processes under development:

(1) IGT-Meissner Process;
(2) Babcock and Wilcox Iron-Oxide Process; and
(3) Air Products Process

IGT-Meissner Process

This process is being developed by the Institute of Gas Technology in conjuction with its U-Gas Process. This process, still in the conceptual stage, utilizes a splashing molten metal-gas contact to remove H_2S from the gas. The contact results in the formation of a metal sulfide which is then decomposed electrolytically to release H_2S and regenerate the molten metal for recycle. The operating temperature is 900°F and a high sulfur removal efficiency (98 percent) is achieved. The exact composition of the molten metal absorbent is proprietary information. The estimated energy requirements

Table 2. High temperature cleanup processes

Basis: 8400 tons/day Illinois No. 6 Coal Fed to BCR Gasifier, or 6700 ppm of Influent H_2S

Process	Absorbent	Type of Bed	Temp. °F	Pressure	Efficiency of S Removal		Absorbent Characteristics				Form of Sulfur Recovery	Energy Required		Status
					% H_2S Influent	Effluent H_2S ppm	Life	Regeneration	Selectivity toward	Make up rate		Elec. kw	Others	
1. Bureau of Mines	Sintered pellets of Fe_2O_3 (25%) and fly ash	Fixed bed	1000 to 1500	Insensitive to variation in pressure	~95	~350	>174 cycles Wt loss < 5%	With air	H_2S, COS	<5%	As SO_2 gas			Pilot
2. Babcock and Wilcox	Fe_2O_3	Fixed bed	800 to 1200	Insensitive to variation in pressure	~99	~75					As 12-15% SO_2 gas			Experimental
3. Consolid. Coal	Half calcined dolomite	Fluidized bed	1500 to 1800	~200 psia H_2S removal is high at low pressure	~95	~350		10-13% with steam and CO_2	H_2S, COS	1% of circulation rate	As H_2S gas to Claus process	98,380		Pilot
4. Air products	Calcined dolomite	Fixed bed	1600 to 2000	Insensitive to variation in pressure			minimum 5-6 cycles	80-90% with steam and CO_2	H_2S, COS		As H_2S gas to Claus process			Abandoned
5. Battelle Northwest	Molten carbonates (15% $CaCO_3$)	Solution	1100 to 1700	Atmospheric H_2S removal is high at low pressure, 5-6 psig	~95	~350		With steam and CO_2	H_2S, COS, fly ash		As H_2S gas to Claus process			Pilot
6. IST - Meissner	Molten metal (proprietary)	Splashing contact	900		~98	~150		Electrolytic	H_2S, COS			8830		Conceptual

given in table 3 are preliminary (ref. 1). Further development is being directed toward establishing mass transfer rates.

Babcock and Wilcox Process

The Babcock and Wilcox Process is similar to the Bureau of Mines' process in that it utilizes iron oxide to remove H_2S from the gas at high temperatures. The difference lies in the material used by the two processes. While the Bureau of Mines' process uses a sintered material made from iron oxide and fly ash, the Babcock and Wilcox process starts out with carbon steel and generates an iron oxide scale on the steel surface which is then used as the desulfurization agent. Briefly, the process chemistry is described by the following reactions:

$$Fe/FeO_X + H_2S \rightarrow Fe/FeS_X + H_2O \qquad (2)$$

At some point in time, all of the available iron oxide scale is converted to the sulfide scale. At that point, the system is regenerated with air as follows:

$$Fe/FeS_X + Air \rightarrow Fe/FeO_X + XSO_2 \qquad (3)$$

The overall process accomplishes two things:

(1) It concentrates sulfur from the raw gas to 10 to 13 volume percent SO_2 in the regenerant gas.

(2) It provides SO_2 in the regenerant gas that is either oxidized to sulfuric acid or reduced to elemental sulfur.

A sulfur removal efficiency greater than 90 percent is claimed by the developers. Absorption can be carried out at temperatures as low as 675°F; however, higher temperatures are desirable for effective regeneration. If regeneration is performed below 1000°F, the sulfide is oxidized to $FeSO_4$ and not to FeO_X. Also, higher temperatures help activate the surface by developing a thick iron oxide layer over which effective absorption occurs; hence, operation is usually at temperatures in excess of 1000°F.

The concentration of H_2S in the desulfurized gas increases as the volume of gas desulfurized on a given iron-oxide scale increases. Therefore, the hardware design for desulfurization and regeneration is one that (ref. 2):

(1) Has a large number of compartments at various stages of regeneration to give an average H_2S concentration in the fuel gas, relatively independent of the regeneration cycle; and

(2) Gives a maximum SO_2 concentration in the regenerant gas.

The hardware that has been designed uses a number of compartments for sulfur removal and the so-called counter-current principle of air regeneration. The desulfurizer uses a modified regenerative type air heater and is referred to as the "regenerative desulfurizer," a schematic of which is shown in figure 1. The cylindrical unit is segmented into 16 compartments. Each compartment is filled with carbon-steel plates oriented longitudinally with the gas flow. The vessel itself will be constructed from high alloy steel.

Table 3. Comparison of operating conditions for fluidized bed combustion and gasification

Operating Conditions	Fluidized Bed Combustion	Fluidized Bed Gasification
Pressure (atm)	10 to 20	10 to 20
Temperature, F	1600 to 1800	1500 to 1700
Gas flow (lb gas/ lb fuel)	~12.5	~5.5
Projected dust loading prior to gas cleanup (gr/scf)	10 to 30	10 to 30
Projected particle size	10 to 25% < 10μ 5 to 15% < 5μ	10 to 25% < 10μ 5 to 15% < 5μ

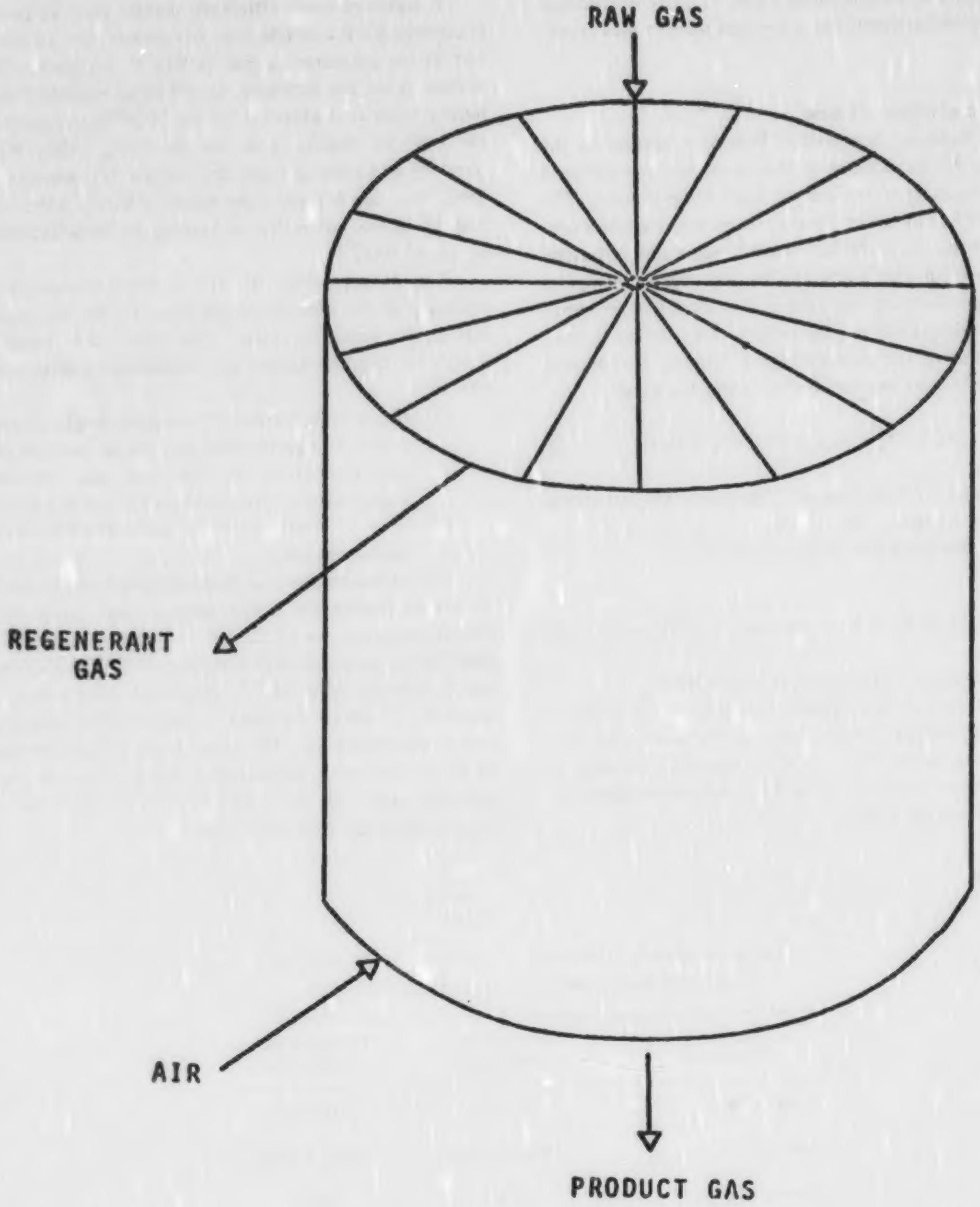

RAW GAS
REGENERANT GAS
AIR
PRODUCT GAS

Figure 1. Regenerative desulfurizer.
(Source: N. J. Kertamus, "Removal of H_2S on Oxidized Iron"
Babcock & Wilcox Research Center)

Desulfurization

Raw gas is passed downward through 13 of the 16 compartments where desulfurization occurs on the surface of the carbon-steel plates. The desulfurized gas issues from the base of the unit and is routed to the combustion device.

Regeneration

The sulfided iron surface is converted back to the oxide in three of the 16 compartments. The regeneration air passes in and upward in the first compartment to a crossover, then downward for a second pass, and upward for a third and final pass. At two revolutions per hour, each of the 16 compartments is regenerated twice per hour. Air enters the first regenerated surface accomplished in the second and third pass downstream. At the end of the first pass, the O_2 concentration is well below 21 percent. During the second pass, the O_2 concentration is further reduced while SO_2 increases. Purging the third (most FeS fouled) compartment with a gas containing a minimum concentration of O_2 and a maximum concentration of SO_2 insures a maximum SO_2 concentration of the final regenerant gas. The regenerant gas should contain 10 to 13 volume percent SO_2.

The effect of temperature on the sulfur concentration in the desulfurized gas is shown in figure 2. This may also be represented by the amount of H_2S removed as a function of the temperature. This is referred to as "sulfur pickup" (figure 3).

The process concept has been demonstrated on bench scale equipment and a hardware design has been developed. The process has yet to be demonstrated on a large scale.

Air Products Process

This process, now abandoned, employed a fixed-bed of fully calcined dolomite to absorb H_2S from the raw gas. The sulfided dolomite was then regenerated with steam and carbon dioxide before being recycled to the absorber. Poor regenerability of the sulfided dolomite led to the abandonment of this process by the Air Products Company.

Factors Affecting High Temperature Cleanup System Selection

Several factors affecting selection of high temperature cleanup systems emerge as the most important in selecting high temperature desulfurization systems for fuel gas cleanup:

(1) Operating temperature;
(2) Capability for removing sulfur compounds, COS, CS_2, as well as H_2S; and
(3) The form in which the sulfur is removed; H_2S, SO_2, or elemental sulfur. Elemental sulfur is the preferred form since it can be stored without significant pollution problems.
(4) Regenerability of the absorbent without substantial loss of activity.
(5) Overall energy requirements and operating costs.

From a qualitative comparison based on the above factors, the Bureau of Mines and the Babcock and Wilcox Iron-Oxide processes appear well suited for use with first-generation gasifiers. These processes are suited for sulfur removal at temperatures below 1500°F, preferably around 1000°F, which is the operating range for first-generation fixed-bed gasifiers. Off-gas from a high temperature second-generation gasifier would require cooling to the operating temperature of the iron-oxide process. This would result in a lower thermal efficiency than for integrated systems using the dolomite based processes, such as the Consol process. A disadvantage of the iron-oxide process is the recovery of sulfur as sulfur dioxide. In order to convert this to elemental sulfur, part of the sulfur dioxide must be reduced to hydrogen sulfide, and this step consumes fuel. The IGT-Meissner process, when developed to the point of commercialization, should also be applicable to first-generation gasifiers, since its operating temperature is about 900°F. The efficiency of sulfur removal for the IGT-Meissner process is estimated at 98 percent, while it is selective toward both H_2S and COS over CO_2.

As previously mentioned, the second-generation gasifiers could employ the Consol dolomite process which has an operating temperature of 1500°F and above. The Battelle molten salt process also operates at temperatures around 1500°F, but its sulfur removal capability is questionable, particularly in the high pressure range.

PARTICULATE REMOVAL SYSTEMS

Particulates of varied sizes, shapes, and composition are: a major contributor to air pollution; a health hazard; and the target of statutory limitations. In addition to their effect on human health, particulates adversely affect pollution control efforts by fouling catalysts used for SO_2 reduction, sulfur recovery, and NH_3 decomposition, etc. Particulates in fuel used for firing gas turbines may cause erosion and/or corrosion of turbine blades. The need for particulate removal from gas streams where they are present in significant quantities cannot be overemphasized.

In order to understand the requirements that must be met by particulate removal systems, an understanding

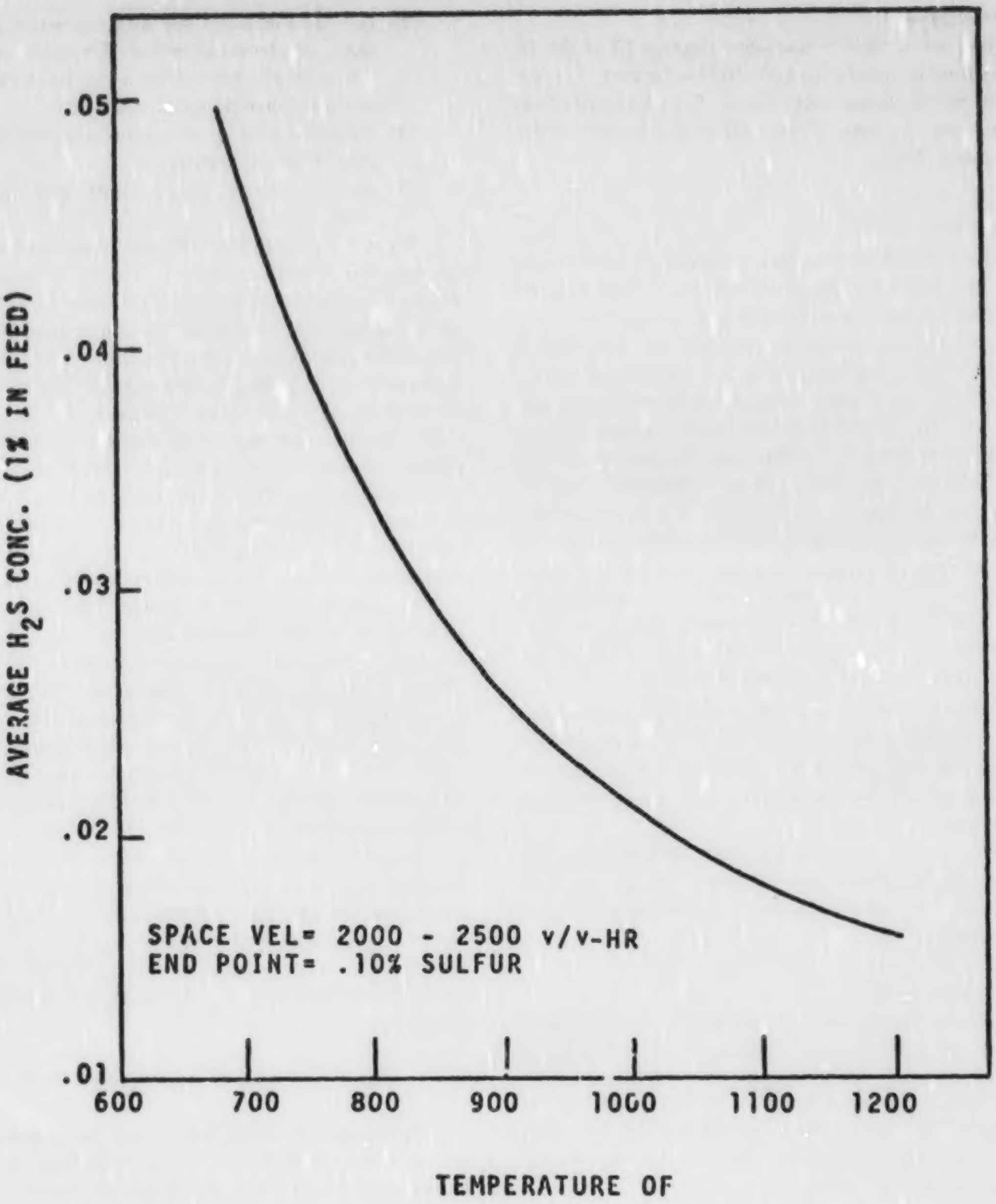


Figure 2. Sulfur concentration vs. temperature.
(Source: N. J. Kertamus, "Removal of H_2S on Oxidized Iron"
Babcock & Wilcox Research Center)

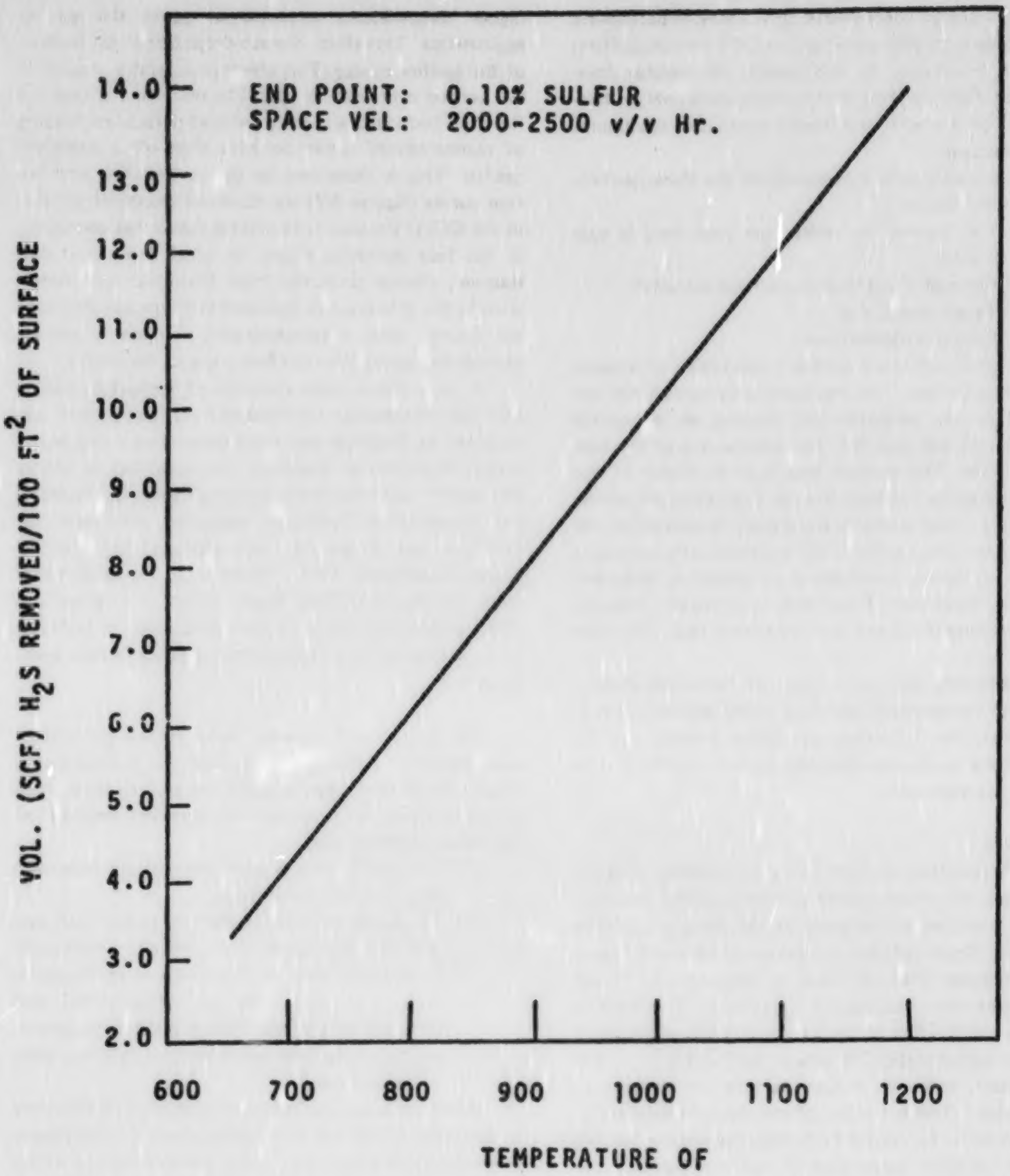


Figure 3. Sulfur pickup.
(Source: N. J. Kertamus, "Removal of H_2S on Oxidized Iron" Babcock & Wilcox Research Center)

of what might be encountered in the way of particulate size distributions and loadings from the various gasifiers must be developed. In this regard, particulates from fixed-bed, fluidized bed, and entrained bed coal gasification will be characterized from a qualitative standpoint in this discussion.

The primary differences between the three gasification methods lie in:

(1) The manner in which the coal feed is supported;
(2) The rate of gas flow (superficial velocity);
(3) Temperature; and
(4) Feed size distribution.

Gas flow rate is the least in a fixed-bed and greatest in an entrained bed. The maximum temperature that can be used in any particular bed depends on the caking properties of the coal fed, the surface area of the coal particles, etc. The surface area is much higher in fluidized and entrained beds than in fixed-beds, therefore, higher temperatures can be employed. Temperatures can generally be raised as the fluidizing/entraining velocity is raised and, hence, are highest in entrained beds and lowest in fixed-beds. Fixed-beds use coarser (heavier) feeds, whereas fluidized and entrained beds use finer feeds.

Considering the three types of beds individually, and using temperature, gas flow rates, and feed size as parameters, the following qualitative analysis can be made of the particulate quantity and size distribution in the fuel gas from each.

Fixed Beds

With fixed-bed gasifiers and their relatively low gas flow rates, the coarser particles tend to settle down, so that the particles carried away by the gas tend to be the finer ones. These gasifiers operate at temperatures (up to 1500°F) lower than ash slagging temperatures. Therefore, the ash does not slag and agglomerate. This leads to a higher ash loading in the gas then if the ash were to slag and agglomerate. The coarse feed (~1/5"), on the other hand, tends to reduce particle entrainment to some extent. The net effect of the three factors, therefore, would be to yield a fairly high particulate loading of finer particles comprised of ash and possibly unburned carbon.

Fluidized Beds

Gas flow rates of fluidized beds are higher than for fixed-beds. Therefore, there is a greater tendency for the bigger particles to be carried away by the gas. Particulate loading in the product fuel gas is also abetted by the finer feed size used in fluidized beds (minus 200 mesh). However, temperature has an opposing effect. The higher temperatures encountered cause the ash to agglomerate. Therefore, the ash drops out of the bottom of the gasifier as slag. This effect reduces the amount of ash carried over with the gas. The net effect is that the fluidized bed yields a slightly reduced particulate loading of comparatively larger particles than off a fixed-bed gasifier. This is illustrated by the particle size distribution curves (figures 4-7) for fluidized bed pyrolysis used in the COED Process. It should be noted that conditions in the four pyrolysis stages, to which the curves correspond, change gradually from fixed-bed type conditions in the first stage to fluidized bed type conditions in the fourth, with a corresponding increase in average particle size going from the first stage to the fourth.

A quantitative approximation of particulate loading and size distribution for fluidized bed gasification was obtained by Westinghouse researchers using a theoretical model developed by Kuniiand Levenspiel (ref. 3) and by comparison with the corresponding figures for fluidized bed combustion. Projected operating conditions for fluidized bed combustion were deduced (by Westinghouse researchers) from experimental data obtained from the National Coal Board (NCB) of England and EPA contractors. The projected conditions for fluidized bed combustion and fluidized bed gasification are given in table 3.

The projected figures for fluidized bed gasification were derived by Westinghouse from the corresponding figures for fluidized bed combustion and the theoretical model of Kunii and Levenspiel taking into consideration the following differences:

(1) The gasification process has less gas flow; less than one-half the air flow.
(2) Fluidizing velocity in the coal gasification system design is about 4 fps, which is one-fourth to one-half that for fluidized-bed combustion.
(3) Ash will essentially be concentrated and removed in the gasification process as agglomerates or slag, and not carried out of the system in the fuel gas.

Based on a qualitative assessment of the differences in the combustion and gasification systems noted above, it is reasonable that a particulate removal system which is designed to handle the dust loading from the fluidized bed combustion process will be able to cope with that from the fluidized bed gasification process.

Entrained Beds

Entrained bed gasifiers have high flow rates and operate at high temperatures (3000°F) with fine feed sizes (minus 200 mesh). In this flow regime the entire feed is carried over; therefore, the particulate loadings

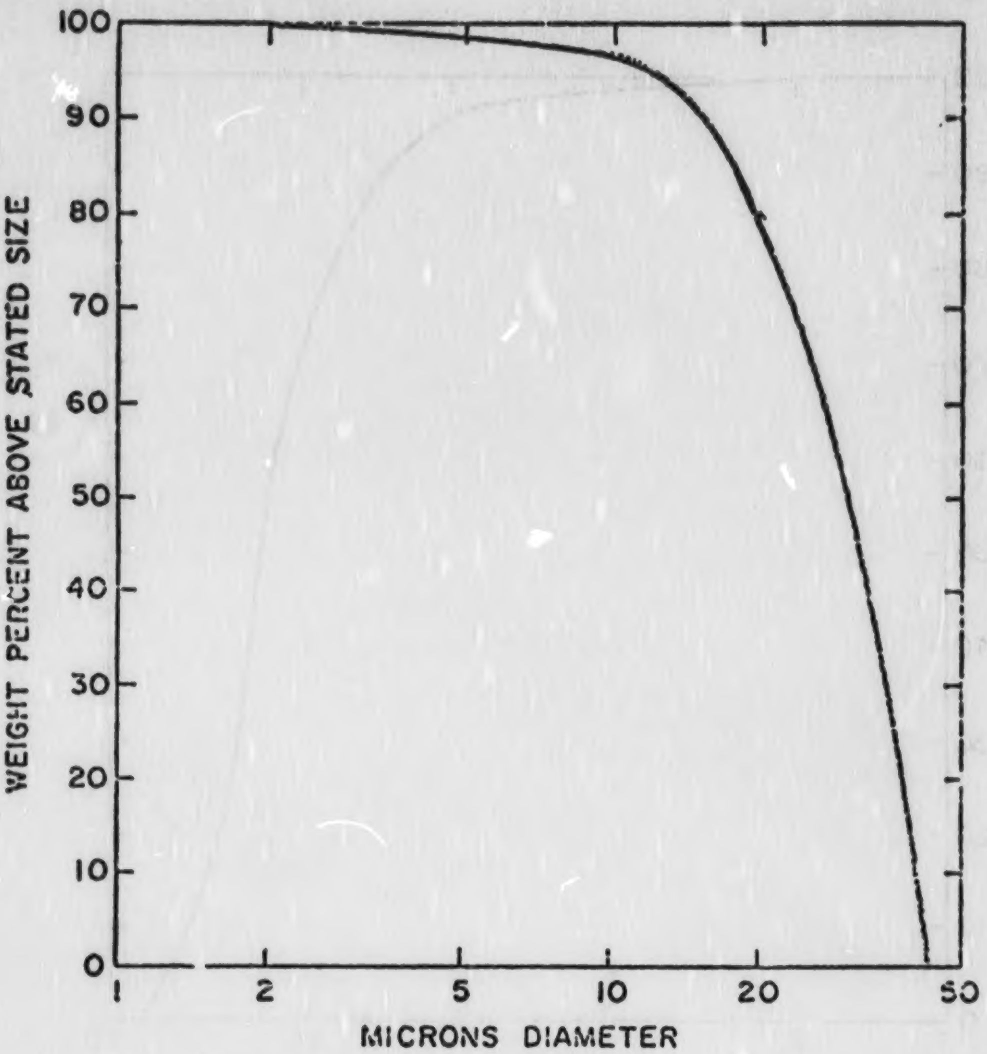


Figure 4. Size distribution of fines from first stage char.
(Source: "Char Oil Energy Development," R&D Report No. 73, OCR,DOI)

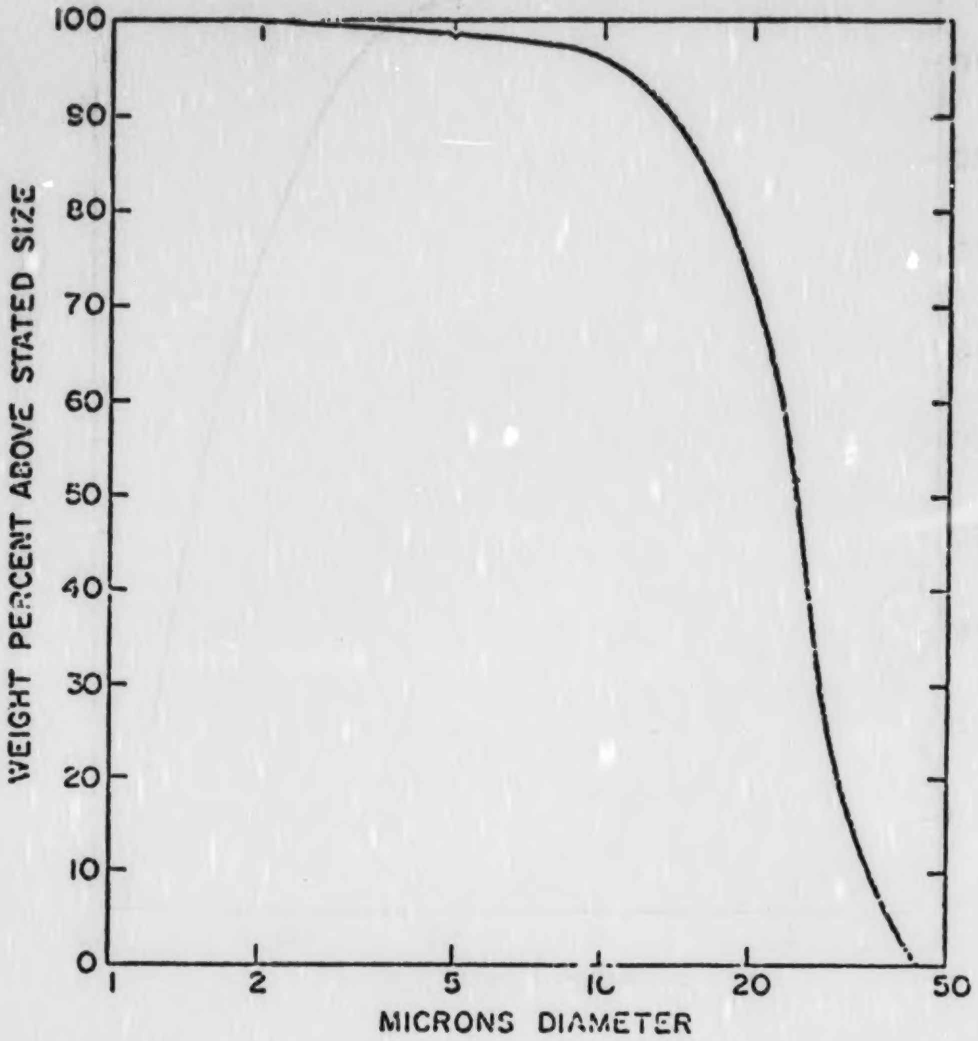


Figure 5. Particle size distribution of fines from second stage char.
(Source: "Char Oil Energy Development," R&D Report No. 73, OCR, DOI)

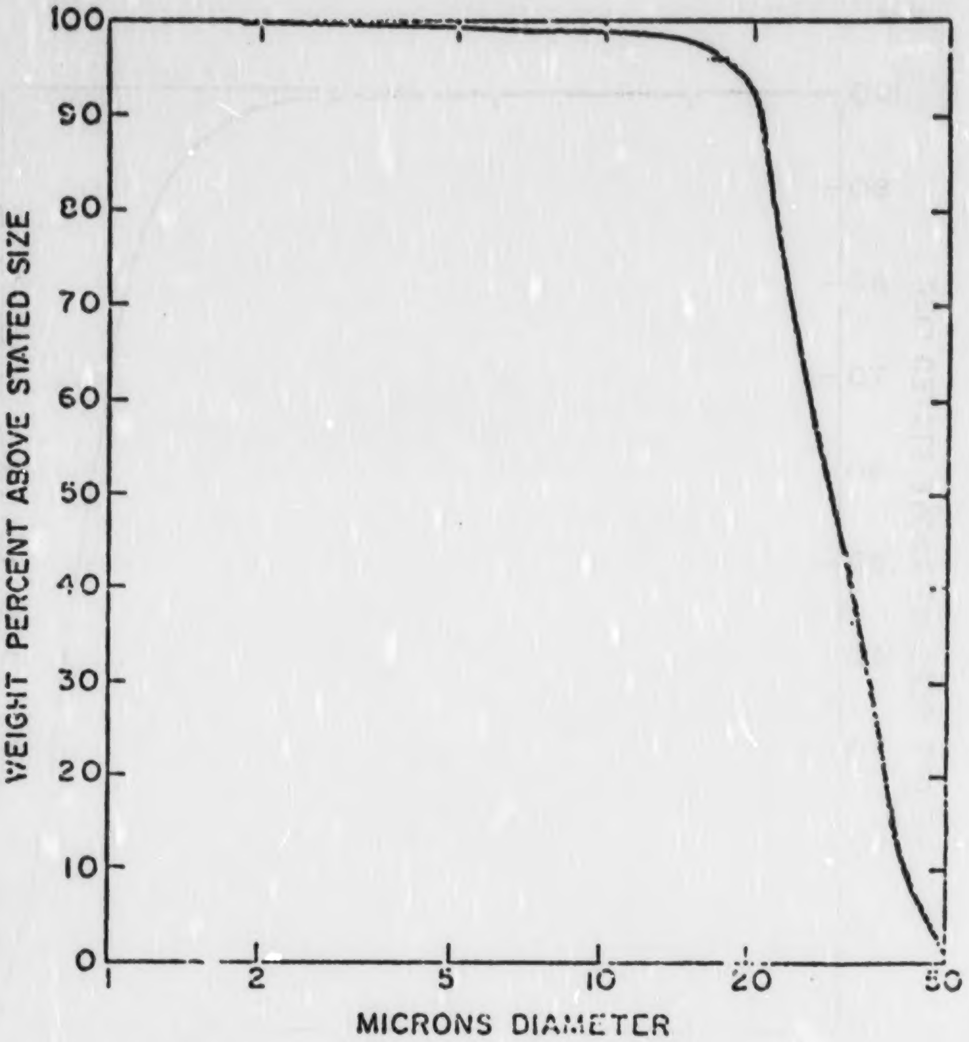


Figure 6. Particle size distribution of fines from third stage char. (Source: "Char Oil Energy Development," R&D Report No. 73, OCR,DOI)

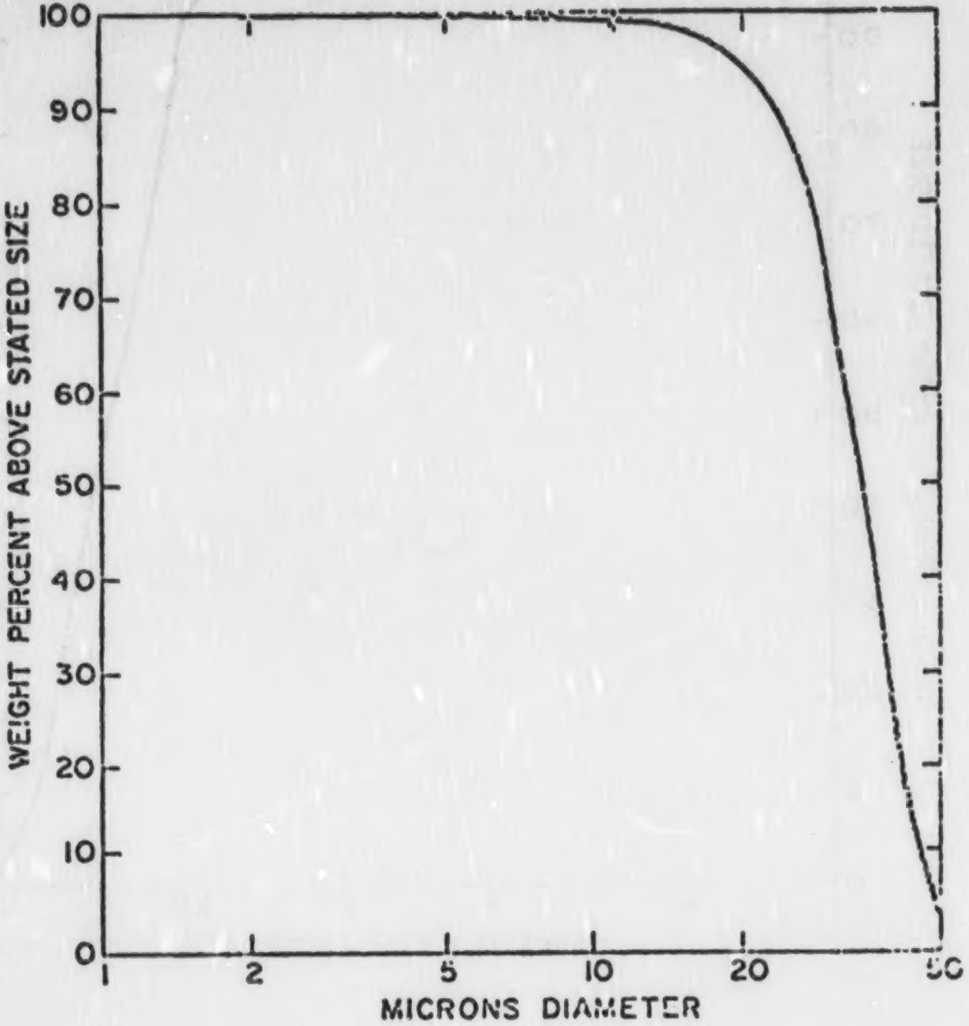


Figure 7. Particle size distribution of fines from product char. (Source: "Char Oil Energy Development," R&D Report N. 73, OCR,DOI)

are very high, with the particle size distribution proportional to the feed size.

Other Factors Affecting Particulate Production and Removal Systems Selection

In all three coal gasification systems discussed above, the particle size distribution and particulate loading are affected by several other factors such as the ash content of the coal, the method of coal preparation, the change in particle density due to chemical reactions, attrition in the bed, and decripitation of particles due to their history. The effects of these factors cannot easily be quantified.

Allowable particulate loadings and size distributions that consider gas turbine requirements as well as air pollution emission regulations have to be considered for the design of particulate removal equipment. Westinghouse (ref. 4) has indicated that particulate loading in the fuel gas being fed to the current generation of gas turbines be limited to no more than 0.01 grains/SCF for particles larger than 2μ, with the total loading not to exceed .15 gr/SCF. Particles less than 2μ are expected to pass through the turbine without impacting the blades.

Many low temperature particulate removal systems are commercially available and descriptions of these are abundant in the literature. Only high temperature systems have been considered for this discussion.

Several high temperature and high pressure particulate removal systems either available or currently under development are listed in table 4. The table includes different types of high temperature particulate removal systems and shows the operating conditions and efficiencies attainable with each.

New Devices

Particularly promising is the moving bed granular filter being developed by the Combustion Power Company (ref. 5). This filter uses a moving sand bed to trap particulates. The filter developer claims a high efficiency (>90 percent) for particle sizes down to 2μ, that the associated pressure drop is relatively low (10 to 15 in H_2O), and that it can be used at high temperatures (1400°F). A current problem area is the disintegration of the filter media. The use of metallic and ceramic media instead of sand is being investigated by Combustion Power Company. Figures 8 and 9 show schematics of the granular filter.

Other promising devices are sonic agglomerators and ceramic filters. These are still largely in the developmental stage. Among the commercially proven devices, cyclones and tornadoes are effective at high temperatures, and are being used in coal gasification pilot plants and process development units.

A literature search will reveal that data on particulate loading and particle size distributions in the off gases from gasifiers are sorely lacking. Considerable effort needs to be directed toward the acquisition of such data if the details of particulate removal systems to protect combined cycle turbines are to be developed.

NO_x CONTROL SYSTEMS

Nitrogen oxides, collectively referred to as NO_x, are an important group of air pollutants. The term NO_x refers primarily to NO (nitric oxide), although similar quantities of NO_2 (nitrogen dioxide) and N_2O (nitrous oxide) may also be formed. These oxides are interconvertible, and the equilibrium between them depends on the action of sunlight, the presence of oxidizing agents, temperature, pressure and other factors. Gas turbines, like other combustion engines, are potentially a major source of NO_x emissions. NO_x is formed in the hot combustion zones of engines. Two known primary mechanisms are responsible for NO_x formation in combustion engines:

(1) Thermal NO_x: Thermal NO_x is formed by the reaction of atmospheric N_2 and O_2 in the hot combustion zone within the engine. This is the dominant mechanism when relatively clean fuels are burned in the engine. Removal of NO_x from flue gases is an extremely difficult problem. However, it is possible to control the thermal NO_x formation by several techniques, some of which are:
   (a) Primary zone leaning by modified combustion chamber design;
   (b) Water injection;
   (c) Exhaust gas recirculation; and
   (d) Reduced turbine inlet temperature.

   Each of the above techniques results in a lower peak temperature within the combustion zone, thereby reducing thermal NO_x formation. The above techniques have their drawbacks, the most important of which is reduced turbine efficiency.

(2) NO_x from fixed nitrogen in the fuel: This source of NO_x is important only when dirty fuels such as coal and residual fuel oil are gasified. Gas produced from these fuels may contain organic nitrogen compounds such as ammonia, hydrogen cyanide, and pyridines. Ammonia is the primary nitrogen compound,

Table 4. High temperature particulate removal systems

Type of removal system	Manufacturer	Capacity ACFM	Collection efficiency %	Minimum particle size with efficiency > 50%, μ	Maximum operating temp. °F	Maximum operating pressure atm	Maximum collection efficiency %	Applicable dust loading range grains/SCF	Pressure drop in. W.G.	Status
Mechanical Collectors										
Cyclones	Buell	50,000	80-90	5-10	1400	2	90-95		4-40	Commercial
	Ducon	58,000	80-90	5-10	1500	10	90-95		4-40	Commercial
Tornado	Aerodyne	30,000	93-97	0.5	1500	10	98	< 30	30	Commercial
Bed Filters										
Granular	Combustion Power Co.		> 90	2	1400		> 90		10-15	Under Development
	Ducon									Under Development
Panel	C.U.N.Y.									Under Development
Rex	Rexnord	20,000	95-99		> 900	1	> 99	< 40	4-15	Commercial
Sonic Agglomeration Collection Systems										
Alternating Velocity Precipitator	Braxton									Under Development
Scrubbers										
Fused salts	Battelle									Under Development
Filters										
Metal and ceramic	Selas and others		> 99	<0.5	2000	1	> 99			Commercial
Electrostatic Precipitators		> 99	< 0.5	800	1	> 99		< 1	Commercial

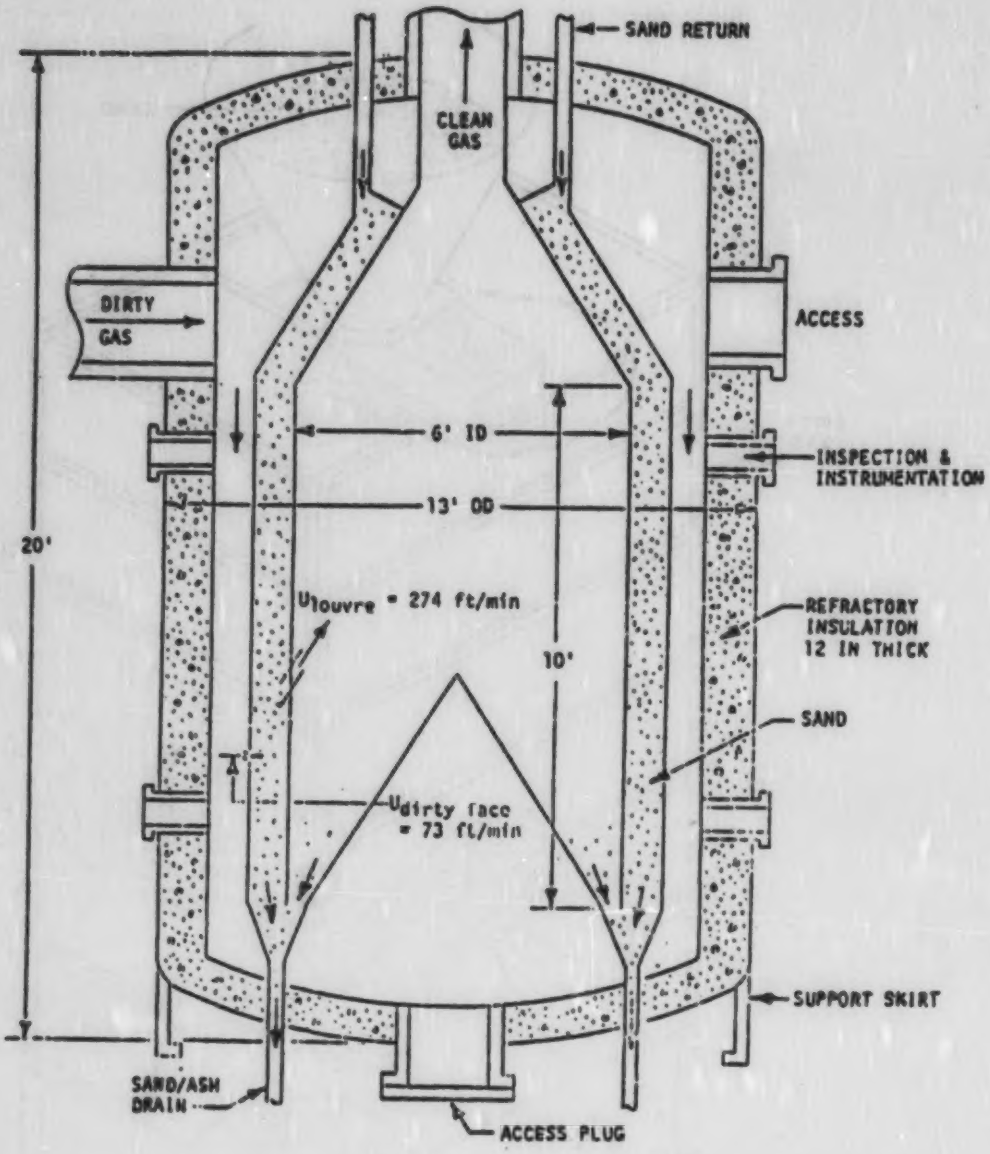

SAND RETURN
CLEAN GAS
DIRTY GAS
ACCESS
6' ID
INSPECTION & INSTRUMENTATION
13' OD
20'
U_{louvre} = 274 ft/min
REFRACTORY INSULATION 12 IN THICK
10'
SAND
$U_{dirty\ face}$ = 73 ft/min
SUPPORT SKIRT
SAND/ASH DRAIN
ACCESS PLUG

Figure 8. Pilot plant granular filter concept.
(Source: Combustion Power Company, Inc.)

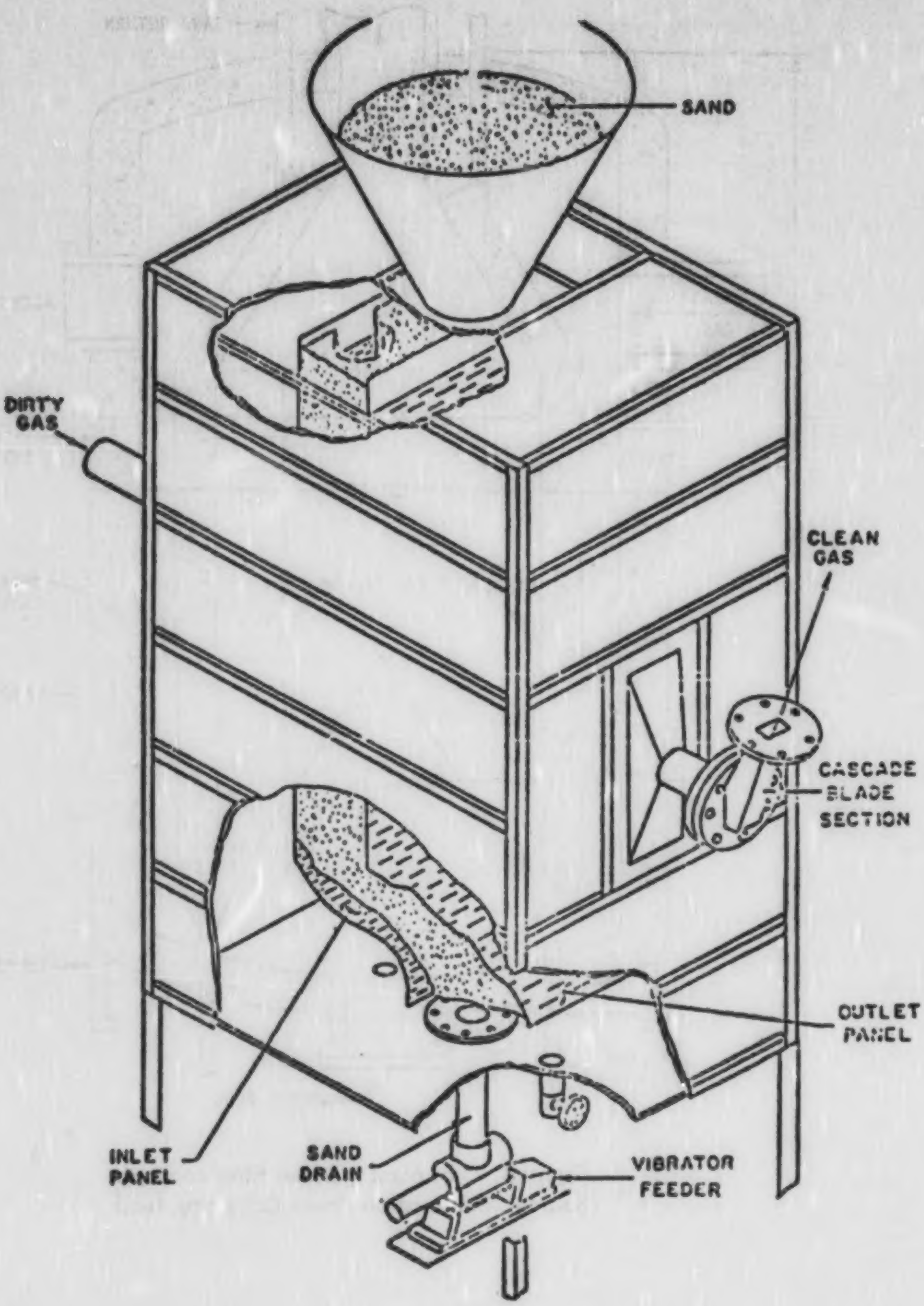

SAND
DIRTY GAS
CLEAN GAS
CASCADE BLADE SECTION
OUTLET PANEL
INLET PANEL
SAND DRAIN
VIBRATOR FEEDER

Figure 9. Model granular filter.
(Source: Combustion Power Company, Inc.)

while the others are present in smaller concentrations. If retained in the gas, these compounds are oxidized during combustion to NO_x. The nitrogen compounds are removed by water scrubbing when a low temperature cleanup system is used. To prevent this carry-through to the turbine, under high temperature cleanup-ammonia and other nitrogen compounds also must be removed from the gas at elevated temperatures. Methods to accomplish this were investigated.

A potential method to remove ammonia is the decomposition of ammonia into stable elemental nitrogen and hydrogen at elevated temperatures. The decomposition of ammonia is governed by the following reaction:

$$2NH_3 \underset{k2}{\overset{k1}{\rightleftarrows}} N_2 + 3H_2 \tag{4}$$

The equilibrium constant k_1 increases as the temperature increases and the total pressure decreases. Temperature has a greater effect than pressure as is verified by the fact that k_1 is practically constant over the pressure range, 1 to 60 atmospheres. Hence the higher the temperature, the greater the decomposition of ammonia into nitrogen and hydrogen. The equilibrium percentage of ammonia in a 3:1 hydrogen gas mixture is shown as a function of pressure and temperature in figure 10.

The equilibrium constants for ammonia formation, $k_p = \frac{k_2}{k_1}$, are tabulated in table 5 (ref. 6) for some temperatures and pressures.

The equilibrium constant for ammonia formation is seen to be very low at high temperatures and low pressures. Under the conditions present in the BCR gasifier (1700° F, 475 psia), the equilibrium ammonia concentration is 200 ppm. However, the actual ammonia concentration is 4260 ppm. This suggests that low equilibrium concentrations, although thermodynamically favored, are not kinetically feasible. Therefore, the decomposition kinetics must be aided by a catalyst.

A literature search will yield considerable recent work in the development of catalysts for ammonia decomposition. General Motors (ref. 7) and Ford Motors (ref. 8) have addressed the ammonia decomposition problem with the goal of ridding automotive exhausts of poisonous nitrogen oxides by first reducing it to ammonia and further decomposing the ammonia to elemental nitrogen and hydrogen. Research in this direction led to the development of several catalysts suitable for ammonia decomposition. Among these are Ni, Pt, W, Mo, Re, and Ru. Of these catalysts, a $Cu\text{-}Ni\text{-}Al_2O_3$ catalyst was seen to have the highest activity for ammonia decomposition. The extent of ammonia decomposition over $Cu\text{-}Ni\text{-}Al_2O_3$ catalyst as a function of temperature is shown in figure 11.

Unfortunately, the above catalysts have a serious drawback. They are poisoned by even trace quantities of sulfur compounds present in the feed gas (ref. 9). The poisoning is due to the formation of a metal-sulfide which deactivates the catalyst. Generally the metal/metal-sulfide equilibrium favors the formation of the metal-sulfide at low temperatures and favors its decomposition at high temperatures. As an example, the poisoning by sulfur compounds of Ni catalyst used in methanation reactions is shown in figure 12. The poisoning effect is seen to diminish only at high temperatures (~2000° F). Effectively, this is the temperature above which, for example, a $Cu\text{-}Ni\text{-}Al_2O_3$ catalyst could be used to decompose ammonia. It is impractical, however, to use the catalyst at this temperature for two reasons:

(1) At such high temperatures, sintering would significantly reduce the activity of the catalyst.

(2) In all the gasification systems considered in the study on which this paper is based, where fuel gas ammonia is significant, fuel gas temperatures approaching 2000° F are unattainable.

The only commercial catalyst potentially capable of decomposing ammonia is an iron oxide catalyst composed of five percent Fe_2O_3 mounted on high temperature fired inert alumina spheres. This catalyst could simultaneously remove H_2S from the gas stream, thus combining the ammonia and sulfur removal operations in a single step. However, the operating conditions necessary for this catalyst are not known and must be determined before the catalyst becomes acceptable (ref. 10).

SUMMARY

In conclusion, it is seen from a state-of-the-art study, that low temperature cleanup systems (operating temperature below 250° F) are commercially available and highly efficient from a pollutant removal standpoint. The fuel gas produced by a fixed bed (low temperature) gasifier contains particulates, condensible tars, phenols, ammonia and other organics. The most convenient scheme for removing the condensibles and particulate involves a liquid quench followed by the separation and recycle of the condensed tar to the gasifier in order to improve thermal efficiency. If a high temperature cleanup system were considered for such an application, it would be faced with the currently unsolved problems associated with high temperature removal of the tars and

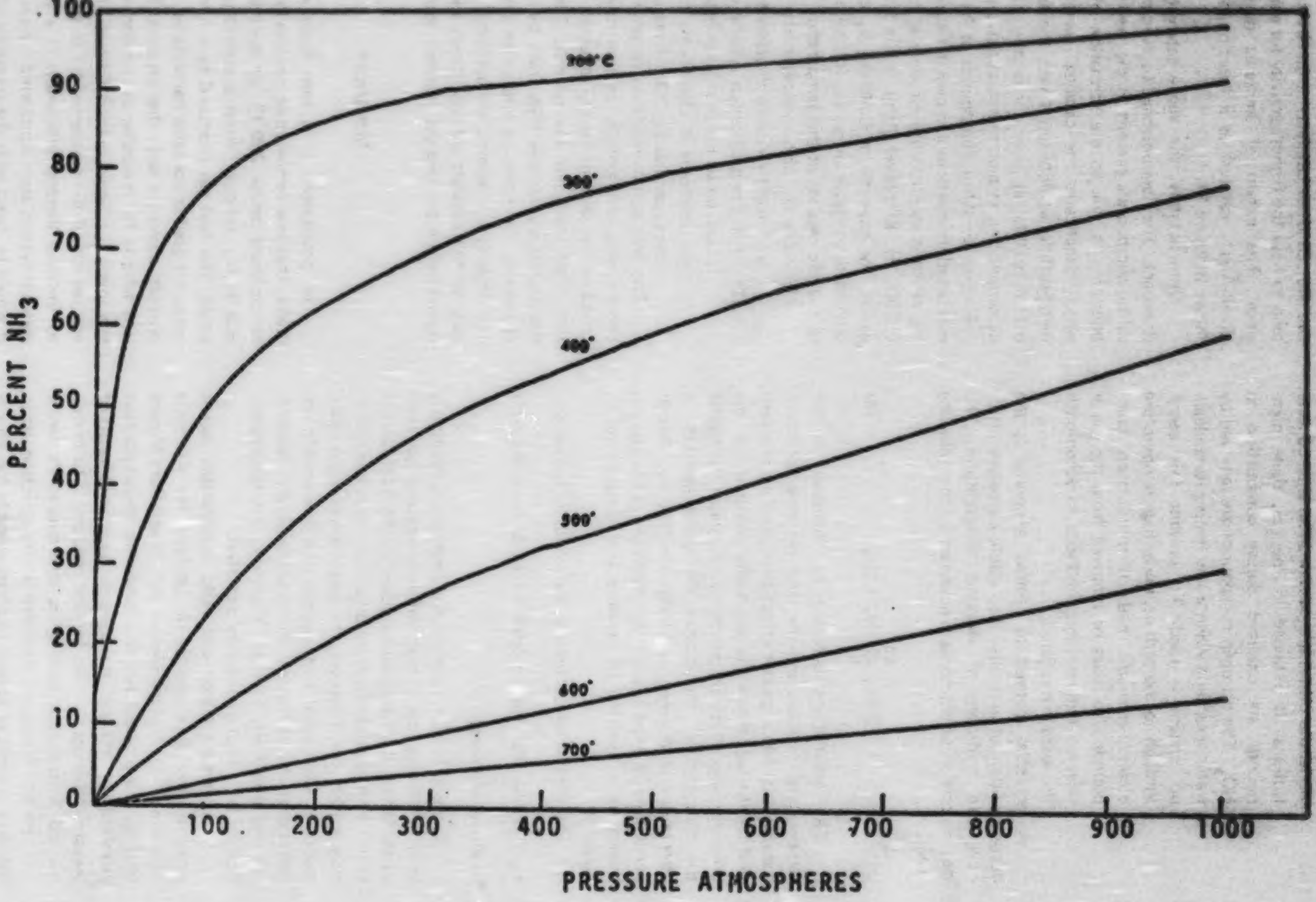


Figure 10. Equilibrium percentage of NH_3 in a 3:1 hydrogen-nitrogen gas mixture.
(Source: G.S. Mitchell, "Ammonia Its Production From Natural Gas," Lion Oil Company)

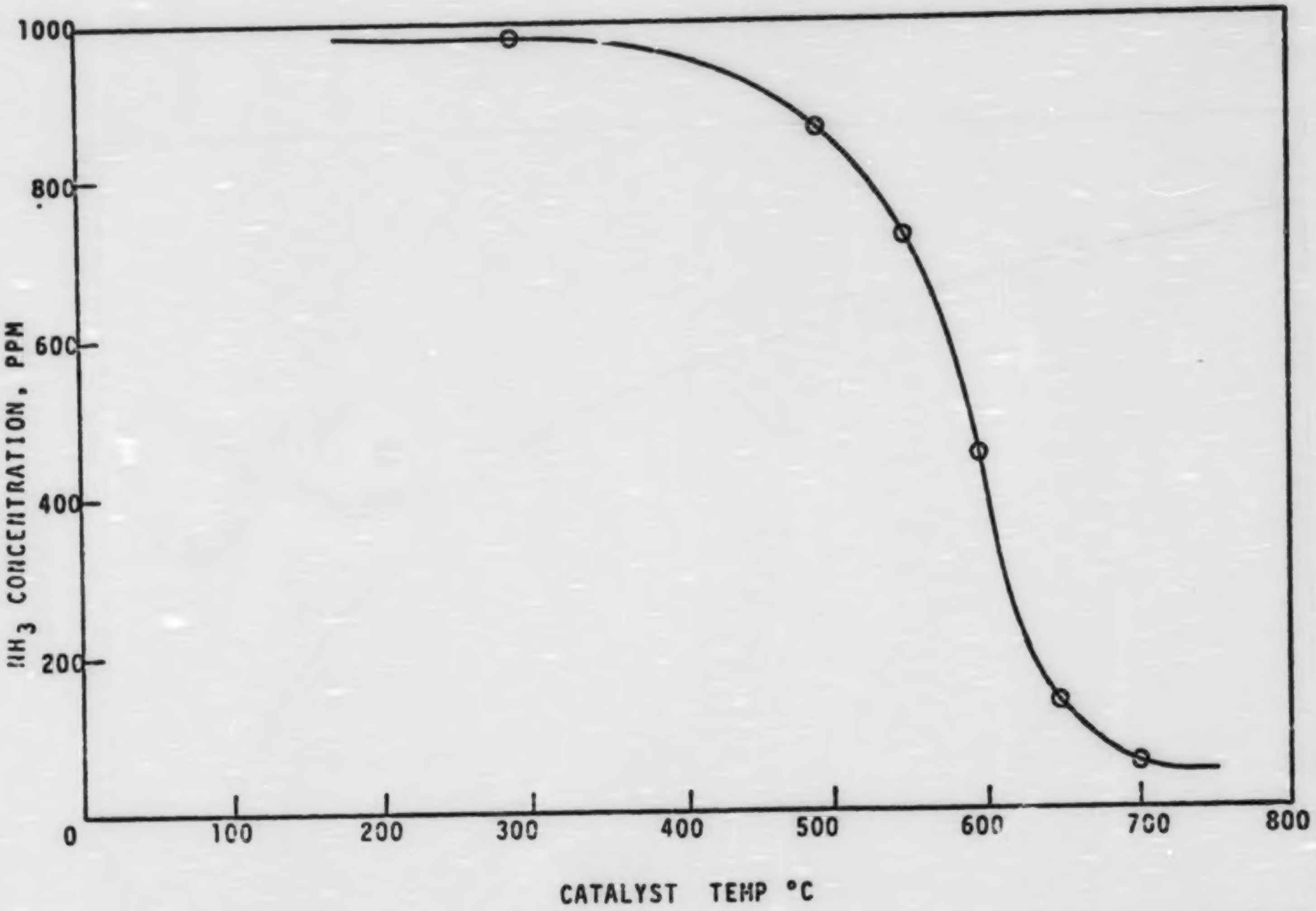


Figure 11. Ammonia decomposition over Cu-Ni-Al_2O_3 catalyst (8.1% Cu, 9.2% Ni). (Source: R.L. Klimisch and K.C. Taylor, "Ammonia Intermediacy as a Basis For Catalyst Selection for Nitric Oxide Reduction," Envir. Sci. & Tech. Vol. 7, No. 2 (Feb. 1973).

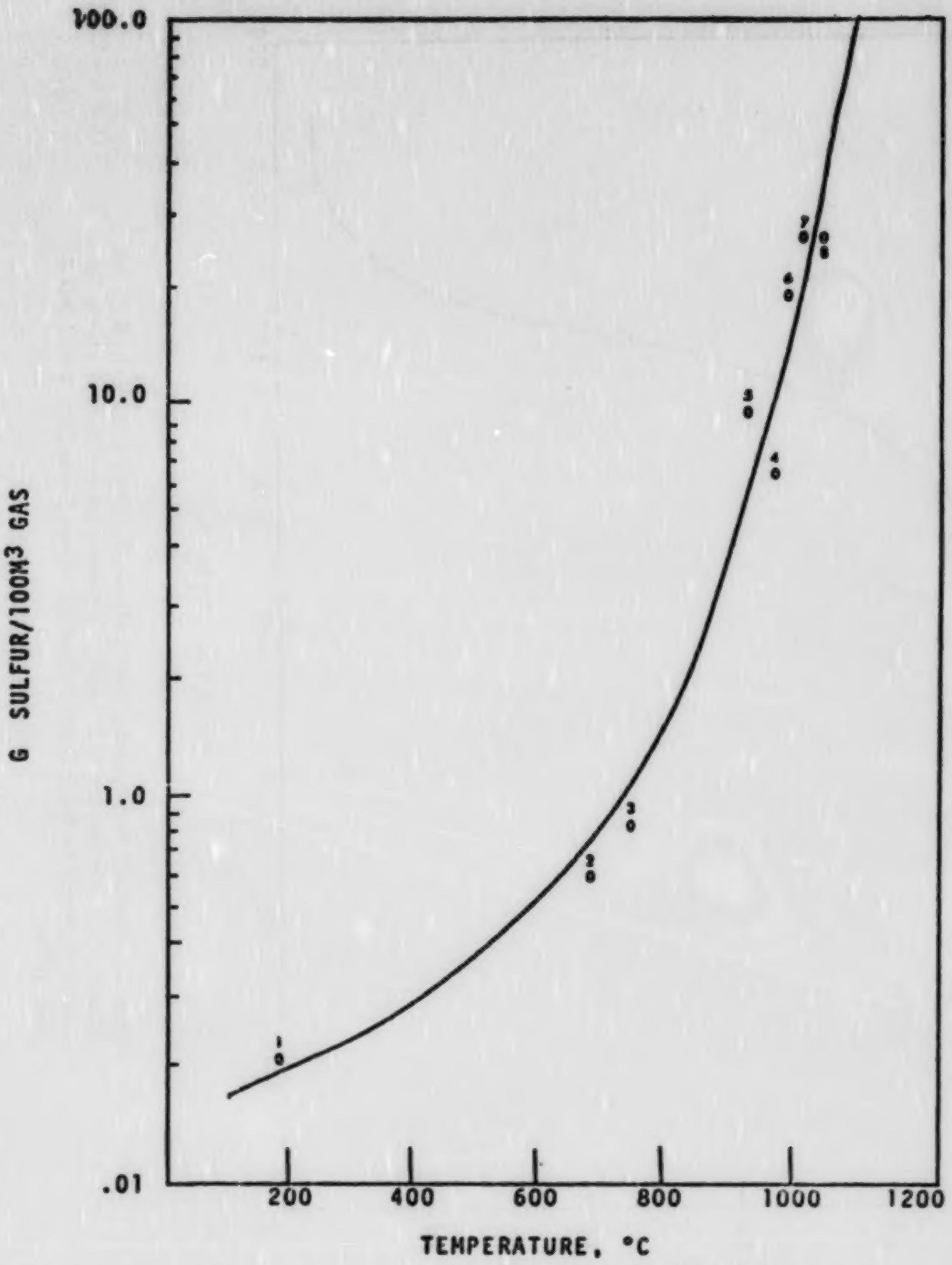


Figure 12. Poisoning of Ni-catalysts used for adjustment of equilibrium:
$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$.
(Source: H. Pichler, "Advances in Catalysis" Vol. 4, Academic Press)

Table 5. Equilibrium constants for ammonia formation

TF	p = 10 atm. kp	p = 30 atm. kp	p = 50 atm. kp
660	0.0266	0.0273	0.0278
750	0.0129	0.0129	0.0130
840	0.00859	0.00876	0.0089

ammonia in the fuel gas. Thus, a low temperature cleanup system is a logical choice for the majority of the gasifiers—specifically fixed-bed gasifiers, like Lurgi, being considered for commercial application. However, a considerable thermal efficiency penalty is associated with the use of the low temperature cleanup systems in combination with coal gasifiers and combined cycle power plants. This penalty has spurred the recent development of high-temperature cleanup systems which make it possible to attain higher thermal efficiencies for the integrated plants. High-temperature cleanup systems are not yet commercially available, and those under development have yet to prove their effectiveness and reliability on a commercial scale.

ACKNOWLEDGMENT

The information on which this paper is based was drawn from work carried out by Hittman Associates, Inc., under contract to the United Technologies Research Center in support of their efforts on EPA Contract 68-02-1099. Some of the information presented in this paper was adapted from previous efforts by the Foster Wheeler Corporation, in their support of the first phase of EPA Contract 68-02-1099. The authors particularly wish to acknowledge the guidance and support provided by the United Technologies Research Center project team headed by Dr. F. L. Robson.

REFERENCES

1. Letter communication, November 15, 1974. Dennis Duncan, Institute of Gas Technology, to M. S. Dandavati, Hittman Associates, Inc.
2. Babcock and Wilcox Research Center, "Removal of H_2S on Oxidized Iron," Kertamus, N.J.
3. D. Kunii and O. Levenspiel, *Fluidization Engineering*, John Wiley and Sons, Inc., 1969.
4. "Clean Power Generation From Coal," R&D Report No. 84, OCR, DOI.
5. Letter communication, December 10, 1974. R. A. Chapman, Combustion Power Company, Inc. to C. B. Colton, Hittman Associates, Inc.
6. S. H. Maron and C. F. Prutton, *Principles of Physical Chemistry*, The Macmillan Company, New York, 1958.
7. R. L. Klimisch and K. C. Taylor, "Ammonia Intermediacy as a Basis for Catalyst Selection for Nitric Oxide Reduction," *Environmental Science and Technology*, Vol. 7, No. 2, February 1973.
8. M. Shelef and H. S. Gandhi, "Ammonia Formation in Catalytic Reduction of Nitric Oxide by Molecular Hydrogen," *Industrial Engineering Chemistry*, Vol. 11, No. 1, 1972.
9. H. Pichler, *Advances in Catalysis*, Vol. 4, Academic Press.
10. Personal communication with Roy Wensink, The Harshaw Chemical Company.

THE BENFIELD ACTIVATED HOT POTASSIUM CARBONATE PROCESS: COMMERCIAL EXPERIENCE APPLICABLE TO FUEL CONVERSION TECHNOLOGY

D. H. McCrea*

Abstract

Activated hot potassium carbonate absorption systems designed and licensed by The Benfield Corporation are widely used for CO_2 *and sulfur compound removal. More than 400 installations are operating or are under construction world-wide. Many are purifying gas streams similar to those that will be generated by the new fuel conversion processes.*

Benfield technology has been thoroughly evaluated for use with these new processes. Detailed designs and recommendations have been prepared for specific proposals in cooperation with major engineering firm licensees. Several research institutes have prepared more general technical and economic evaluations, with Benfield's cooperation, for EPA, ERDA, TVA, and other governmental and private organizations. Some of their reports are available to the public. Benfield reports outlining process performance and economics are also available.

While the applicability of Benfield technology to fuel conversion processes has been established, each application requires individual evaluation. Integration of purification into the overall process and meeting environmental standards require careful consideration.

BENFIELD ABSORPTION PROCESSES

Description

The Benfield Activated Hot Potassium Carbonate Process is a liquid absorption system for the removal of CO_2 and sulfur compounds. Absorption is accomplished in conventional packed or trayed towers, normally at an elevated pressure, and at temperatures up to about 270° F by contact with an aqueous solution containing 25 to 35 percent K_2CO_3 along with small quantities of an inorganic corrosion inhibitor and an organic or inorganic activator to catalyze the rates of absorption and desorption. Absorbed components are recovered in a second tower by contact with a stripping gas, usually steam supplied from a process gas or steam heated solution reboiler. The arrangement is illustrated in figure 1. In practice, however, other configurations are often used to achieve higher degrees of purification, to satisfy specific process requirements, and to minimize capital and operating costs. Some of these modifications have been discussed in earlier Benfield reports (refs. 1-5).

Removal and recovery of CO_2, H_2S, mercaptans and other acidic components occur due to reversible chemical reactions with K_2CO_3:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3,$$
$$K_2CO_3 + H_2S = KHCO_3 + KHS,$$
$$K_2CO_3 + RSH = KHCO_3 + KRS.$$

The organic sulfur compounds, COS and CS_2, do not react directly with K_2CO_3, but are instead hydrolized to H_2S and CO_2:

$$COS + H_2O = CO_2 + H_2S,$$
$$CS_2 + 2H_2O = CO_2 + 2H_2S.$$

Hydrolysis is catalyzed by the solution and proceeds orders of magnitude faster than in water. Aside from acidic gases and gases that can hydrolize, the compounds found in raw gas are, with few exceptions, unreactive with the solution.

Background

The hot potassium carbonate process was developed by Benson, Field, and coworkers at the U. S. Bureau of Mines (now a part of ERDA) in the early 1950's (refs. 6-9). Their work was prompted by the need for an improved process to purify moderate to high pressure coal-derived synthesis gas and demonstrated the technical feasibility of the process as well as its advantages over other available technology. For many applications, the hot carbonate process requires much less thermal energy than amine scrubbing systems (ref. 10) and significantly lower capital investment than processes using physical solvents (ref. 11). Other advantages, compared to either amine or solvent scrubbing, include use of nonvolatile, lower cost, chemically stable solution, reduced solubility of process gas, and higher temperature operation.

The economics of the hot carbonate process has been improved and its range of applicability extended through research conducted by The Benfield Corporation. Significant developments include:

1. Introduction of more effective corrosion inhibitors and control methods (ref. 12) which allow mostly carbon steel construction.
2. Development of activators to improve kinetics and alter equilibria relationships (ref. 13) so that tower sizes can be reduced, higher gas purities obtained, and thermal efficiency increased.
3. A multizone tower design (ref. 14) that reduces

---

*The author is with The Benfield Corporation, Pittsburgh, Pa.

Preceding page blank

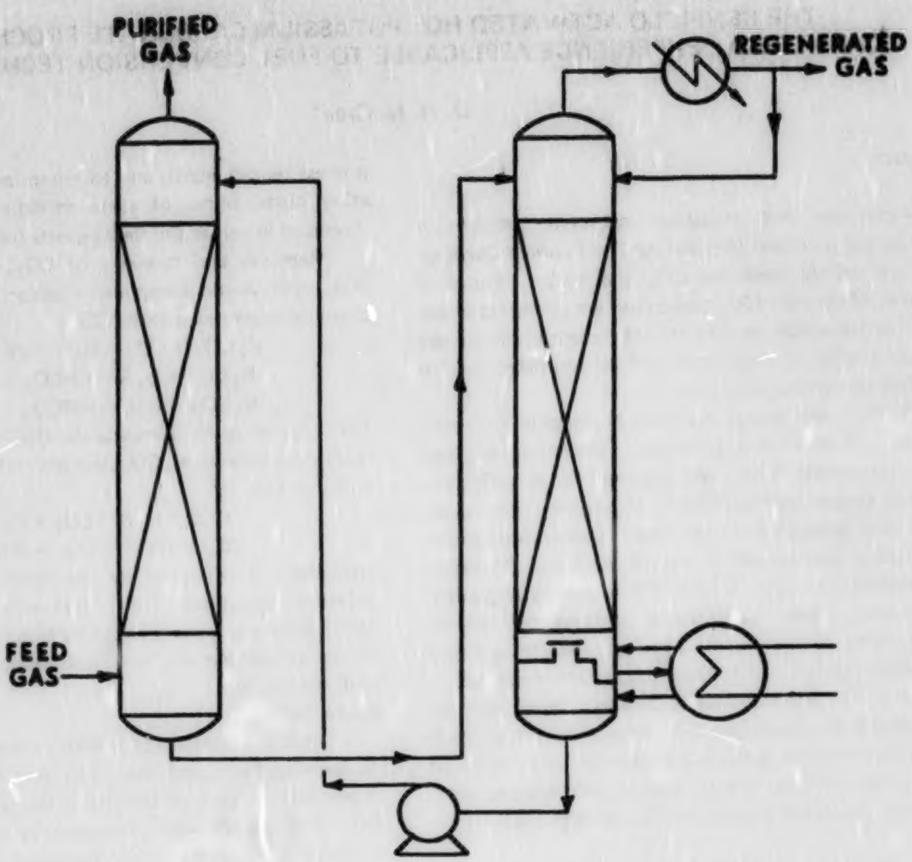


Figure 1. Simplified flow diagram of the Benfield activated hot potassium carbonate process (single stage design).

absorber diameter and lowers investment cost for high pressure service.

4. Flowsheet modifications (ref. 15) to improve thermal efficiency.
5. A process configuration (Benfield HiPure Process) (ref. 4) by which purified gas containing less than 1 ppm H_2S and 10 ppm CO_2 can be obtained.
6. A process configuration permitting selective absorption of sulfur compounds from an excess of CO_2.
7. Characterization of performance parameters for tower packings at commercial operating conditions (ref. 16) allowing more accurate designs and reduced tower sizes.

Experience

Benfield technology is offered worldwide through licensing agreements with most of the major engineering-construction firms. More than 400 Benfield designed systems have been built or are under construction. Principal applications have been purification in the production of:

Town Gas
Ammonia
Hydrogen
SNG from naphtha
Ethylene oxide
Vinyl acetate

Benfield systems have also been used for the purification of natural gas and of gases produced by partial oxidation or coal gasification. Experience in these applications is of particular interest in evaluating use of Benfield technology in the new fuel conversion processes since the gas streams are, in many respects, similar.

The Benfield Process was used for over 13 years to treat raw gas made from coal by the Lurgi Process at Westfield, Scotland (ref. 17). Contaminants in the gas were not harmfully reactive with the solution, there was no significant corrosion, and efficient removal of both H_2S and organic sulfur was obtained. Similar success has been achieved in eight applications treating sulfur-containing gas produced by partial oxidation of heavy oil and in 11 applications where natural gas containing both CO_2 and H_2S is being purified. In one of these, the H_2S content of the gas is being reduced from 12 percent to less than 1 ppm.

Operating data for some of these units are summarized in table 1. While the table illustrates conditions at which Benfield technology has been demonstrated, it does not indicate the degree of gas purity obtainable. In most cases, the units were designed to most economically meet predetermined criteria rather than to achieve maximum gas purity.

EVALUATION OF BENFIELD TECHNOLOGY FOR USE IN FUEL CONVERSION PROCESSES

Scope of Studies

The integration of Benfield technology into fuel conversion processes has been extensively studied in cooperation with engineering firm licensees, for many specific proposals. These have included:

Production of pipeline gas from coal or heavy oil
Production of liquids from coal
Production of low and medium Btu gas from coal or heavy oil
In situ coal gasification
Oil shale processing
Geothermal power generation
Fuel cell processes.

Studies conducted for licensees are, of course, confidential. Some of the results, however, have been included in a Benfield report (ref. 5) that can be used to estimate capital cost and utility consumption, thus serving as a guide to process developers in making preliminary evaluations of specific applications.

A number of independent evaluations of fuel conversion processes including Benfield purification have also been conducted. Benfield has been privileged to cooperate in these studies which have been mainly sponsored by governmental research organizations. A partial list of evaluations is shown in table 2. In at least some cases, reports are publicly available.

Conclusions

Utilization of Benfield technology in the new fuel conversion processes does not appear to present a major engineering challenge at least in satisfying the process needs of gas purity and reliability. All of the requirements have been demonstrated on an industrial scale.

1. Trace components expected in the raw gas have been successfully handled without undo chemical or mechanical problems.
2. Pressures expected are in the range of industrial experience. Large systems have operated at 1100 psig.
3. Ability to treat the large volumes of gas expected has been demonstrated. For example, the gas produced in a 250 MM SCFD based SNG plant can be treated in three Benfield trains without exceeding commercially demonstrated equipment size. Scale-up to a two-train plant should present no problems.
4. Achieving required gas purity from CO_2 and H_2S has been demonstrated. Organic sulfur removal to the level needed for catalyst protection has not been achieved industrially because there has been no need. However, commercial results have confirmed the design parameters for organic sulfur removal and have demonstrated that levels now required are obtainable.

In satisfying the requirements for specific applications, the principal design goals are usually to:

1. Minimize capital investment
2. Achieve maximum thermal efficiency by best utilizing available low level heat
3. Assure stable operation and avoid the possibility of CO_2 or sulfur breakthrough in the event of plant upsets
4. Satisfy environmental emission limits

Even though process objectives can readily be achieved and design goals have been reasonably well established, specifying the purification system still requires

Table 1. Partial list of Benfield units purifying natural gas or gas produced by partial oxidation or coal gasification

Application	Capacity MMSCFD	Pressure psig	Raw Gas Analysis		Pure Gas Analysis	
			CO_2	H_2S	CO_2	H_2S
Natural Gas	150	1100	7%	16%	1%	.05%
Natural Gas	165	1000	12.3%	.8%	.5%	20 ppm
Natural Gas	330	1000	16%	50 ppm	1%	<1 ppm
Natural Gas	31	600	42%	12%	.1%	<1 ppm
Natural Gas	18.5	600	7%	1%	.2%	4 ppm
Natural Gas	60.5	600	24%	20 ppm	1%	nil
Partial Oxidation	21.9	370	33%	.06%	.4%	<1 ppm
Partial Oxidation	6.4	140	26%	1%	110 ppm	<1 ppm
Partial Oxidation	52.1	440	5.2	.93%	.95%	45 ppm
Coal Gasification	23.9	325	28%	.6%	.8%	70 ppm

ingenuity and careful study. The many evaluations for specific projects conducted by Benfield and by others have demonstrated that:

1. Purification must always be considered as an integral part of the overall process. Location and characteristics of the purification step or steps can significantly influence the selection, cost, and reliability of both upstream and downstream units.
2. Environmental criteria will influence the economics of the purification system and may even determine the process sequence specified.

Two examples, illustrating the effects of sulfur emission standards on design, are given in the concluding section of this report.

INFLUENCE OF EMISSION STANDARDS ON SPECIFYING BENFIELD SYSTEMS

Production of Pipeline Gas

One design situation often encountered is the gasification of a high sulfur coal by a process producing a relatively low quantity of CO_2 so that the CO_2 to sulfur ratio in the raw gas is less than about 8 to 1. A processing sequence as illustrated in figure 2 would be specified. By removing sulfur and CO_2 prior to shift conversion, a gas suitable for Claus processing, which is more economical than systems suited to dilute streams, can be used for final sulfur recovery. With this sequence, the most economical approach is to design the first stage of Benfield purification for nearly 100 percent H_2S removal but not to attempt complete organic sulfur removal. The residual organic sulfur is removed in the second stage of Benfield purification and appears as H_2S, typically 20 to 50 ppm, in the CO_2 stream. If this H_2S level is not permissible, the increased investment cost of complete sulfur removal in the first Benfield stage must be compared to recovering sulfur from the CO_2 vent stream or for oxidizing the H_2S to SO_2.

Production of Fuel Gas

The effect of sulfur emission standards on the investment cost and thermal efficiency of Benfield purification systems is more easily seen in cases where sulfur removal is only an environmental requirement and is not required for the process. One case evaluated recently was selective desulfurization of fuel gas produced by partial

Table 2. Partial list of independent studies of fuel conversion process which include Benfield purification

Organization	Sponsor	Subject
Air Products and Chemicals	OCR	Pipeline gas
Babcox and Wilcox	EPRI	Low Btu gas
Battelle Memorial Inst.	EPA	Pipeline gas
Battelle Memorial Inst.	TVA	Low Btu gas
Beard Engineering	Municipality	Combined power cycles
Bituminous Coal Research	OCR	Pipeline gas
Braun	OCR-AGA	Pipeline gas
Chem Systems	OCR	Pipeline gas
City College of City University of New York	City College of City University of New York	Combined power cycles
Dravo	ERDA	Pipeline and low Btu gas
Exxon Research and Eng.	ERDA	Pipeline gas
General Electric	EPRI	Fuel Cells
Institute of Gas Tech.	OCR	Pipeline gas
Institute of Gas Tech.	EPA	Low Btu gas
Koppers	OCR	Pipeline and low Btu gas
NASA	NASA	Combined power cycles
Procon	OCR	Pipeline gas
Swindell-Dressler	OCR	Low Btu gas
TVA	EPRI	Low Btu gas
U.S. Bureau of Mines	Bureau of Mines	Low Btu gas
U.S. Bureau of Mines	Bureau of Mines	In situ gasification
Westinghouse Electric	OCR	Combined power cycles

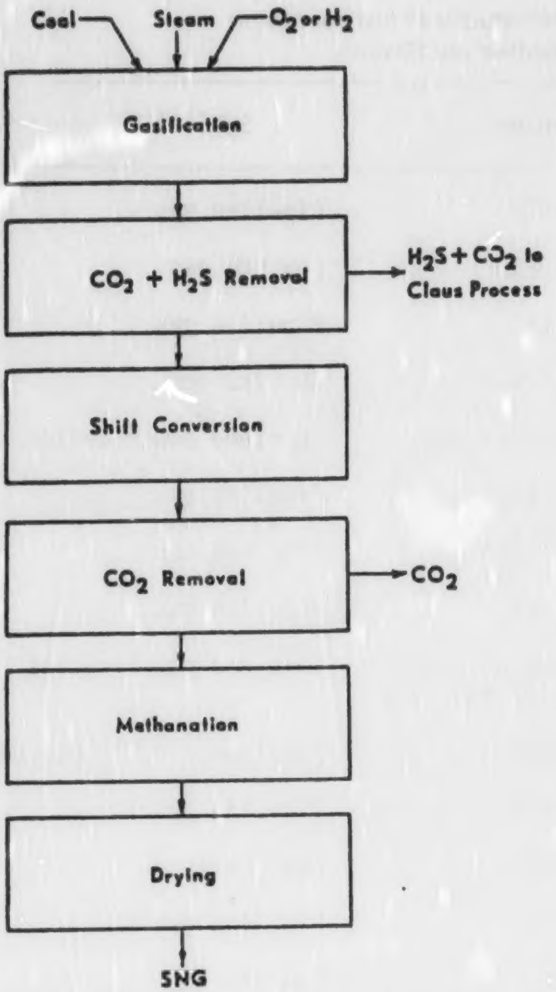


Figure 2. Benfield purification in an SNG from coal process: acid gas removal before and after shift conversion.

oxidation. Investment cost, energy requirement, and dilution of the H_2S stream for Claus processing are all dependent on the degree of desulfurization required (see table 3).

As emission restrictions become more stringent, both the investment cost and energy needs of the Benfield system increase. In addition, the H_2S content of the feed stream to elemental sulfur recovery decreases, thus increasing the cost and reducing the efficiency of this unit. The data for the 40 and 50 ppm designs show the effect of a change in unit configuration trading off investment for reduced energy consumption.

When producing a low Btu gas, perhaps 125 Btu/NCF, the energy consumed for purification is a significant portion of the total available and is strongly dependent on emission standards. The imposition of standards more stringent than for an equivalent direct coal-fired system with flue gas cleanup could affect the economic feasibility of projects for fuel gas production.

REFERENCES

1. D. H. McCrea and H. E. Benson, "Benfield Processes for SNG and Fuel Gas Purification," 165th American Chemical Society National Meeting, Dallas, Texas, April 8-13, 1973.
2. R. W. Parrish and J. H. Field, "The Benfield Process in Coal Gasification," 24th Annual Gas Conditioning Conference, The University of Oklahoma, Norman, Oklahoma, March 14-15, 1974.
3. R. W. Parrish and H. B. Neilson, "Synthesis Gas Purification Including Removal of Trace Contaminants by the Benfield Process," 167th American Chemical Society National Meeting, Los Angeles, California, March 31-April 5, 1974.
4. H. E. Benson and R. W. Parrish, "HiPure Process Removes CO_2/H_2S," *Hydrocarbon Processing, 53, 4*, pp 81-2.
5. D. H. McCrea and J. H. Field, "The Purification of Coal Derived Gases: Applicability and Economics of Benfield Processes," 78th American Institute of Chemical Engineers National Meeting, Salt Lake City, Utah, August 18-21, 1974.
6. H. E. Benson and J. H. Field, "Method of Separating CO_2 and H_2S from Gas Mixtures," U. S. Patent 2,886,405, May 1959.
7. J. S. Tosh, J. H. Field, H. E. Benson, and W. P. Haynes, "Equilibrium Study of the System Potassium Carbonate, Potassium Bicarbonate, Carbon Dioxide, and Water," Bureau of Mines Report of Investigations 5484, 1959, 23 pp.
8. J. S. Tosh, J. H. Field, H. E. Benson, and R. B. Anderson, "Equilibrium Pressures of Hydrogen Sulfide and Carbon Dioxide over Solutions of Potassium Carbonate," Bureau of Mines Report of Investigations 5622, 1960, 25 pp.
9. J. H. Field, H. E. Benson, G. E. Johnson, J. S. Tosh, and A. J. Forney, "Pilot Plant Studies of the Hot Carbonate Process for Removing Carbon Dioxide and Hydrogen Sulfide," Bureau of Mines Bulletin 597, 1962, 44 pp.
10. Benfield Corporation, "The Way to Low Cost Scrubbing of CO_2 and H_2S from Industrial Gases," 1970, 11 pp.

Table 3. Influence of emission standards on purification cost and utility requirement

Sulfur in Purified Gas ppm	H_2S in Claus Feed %	Investment $/1000 NCFD Feed	Energy Required Btu/NCF
750	22.9	12.53	6
210	19.7	13.13	10
100	-	15.35	11
50	-	17.16	15
40	17.1	29.16	13

11. Benfield Corporation, "Low Cost Reliable Systems for the Removal of Acid Gases from Ammonia Synthesis Gas Trains Based on Partial Oxidation of Fuel Oil," 1974, 13 pp.
12. Joseph H. Field and Donald H. McCrea, "Method of Removing Carbon Dioxide From Gases," U.S. Patent 3,863,003, January 1975.
13. Joseph H. Field, "Separation of CO_2 from Gas Mixtures," U.S. Patent 3,907,969, September 1975.
14. H. E. Benson, "Separation of CO_2 and H_2S from Gas Mixtures," U. S. Patent 3,563,695, Feb. 1971.
15. H. E. Benson, "Separation of CO_2 and H_2S from Gas Mixtures," U. S. Patent 3,823,222, July 1974.
16. L. J. P. Evans and Q. M. Siddique, "CO_2 Removal Studies and Their Application to SNG Plant Conversions," IGE Autumn Research Meeting, London, England, Nov. 25-26, 1975.
17. T. S. Ricketts, "The Operation of the Westfield Lurgi Plant and High Pressure Grid System," The Institution of Gas Engineers 100th Annual General Meeting, London, England, May 14-17, 1963.

COAL CONVERSION PROCESS WASTEWATER CONTROL

W. A. Parsons and R. A. Ashworth*

Abstract

Wastewater contributions are generated from various unit operations incorporated in the process sequence of coal conversion plants. Such discharges are potentially highly pollutional unless wastewater control is engineered into the production facility. This paper identifies the principal wastewater generating processes and describes the magnitude and characteristics of the effluents expected from various coal conversion processes. Process-oriented effluent control alternatives are presented that exploit the prospects for process revision, recovery, recycle and serial reuse. Treatment-oriented effluent control concepts are analyzed for applicability to wastewater disposal situations. Technical problems associated with the implementation of wastewater control are discussed. The expected performance of the wastewater control concepts are evaluated in terms of contributions of pollutants and residuals.

Wastewater control is a factor of great significance in the siting, engineering and operation of major coal conversion plants. Maximum water conservation will be mandated in the design of coal conversion plants located in coal reserve areas with limited water supply. Exemplary wastewater control will be required to obtain NPDES permits for plants discharging process effluent or contaminated runoff to natural watercourses. Water quality limited situations could result in site specific effluent requirements. In addition, it is to be expected that applications for discharge permits will receive close scrutiny by fish and wildlife agencies, conservation groups and the public, relative to possible environmental impacts from the array of pollutants generated by coal conversion processes. Protracted delays in project implementation have occurred as a result of these considerations.

Stringent wastewater control requirements pose challenges of legion proportions to design engineers because of uncertainty as to: (a) the wastewater characteristics, (b) the performance of wastewater control technology and (c) the discharge permit requirements. Wastewater characteristics will differ with the particular coal conversion process selected for application and with the characteristics of the coal feed. Few modern, high pressure, coal conversion plants are available to provide definition of wastewater characteristics, but some information is available from foreign installations and from experimental units. In cases where a preview projection must be made, expediency may require the speculative synthesis of wastewater characteristics based upon somewhat analogous effluents from byproduct coke plants.

Information on the performance of process-oriented and treatment-oriented wastewater control technology is sparse — particularly at the stringent levels of abatement associated with new point source discharge standards. Information on the performance of wastewater control technology at byproduct coke plants is available for conceptual guidance in analogous situations, but presently demonstrated control technology will rarely meet new point source discharge standards without additional process development. Since process development requires identification of problem areas and screening of alternatives, the object of this paper is the presentation of a generalized overview of sources of wastewater plus process oriented and treatment-oriented alternatives for wastewater control.

SOURCES AND CHARACTERISTICS OF WASTEWATER

Storm-Generated Wastewater

Wastewater control involves consideration of process wastes and contaminated runoff. A generalized schematic illustrating wastewater sources from coal conversion processes is given as figure 1, where it is evident that wastewater control commences at the coal supply and storage areas. Runoff from coal receiving, unloading and from coal processing areas may require collection and treatment prior to discharge — especially if receiving waters are water quality limited. The expected characteristics of the runoff are undefinable inasmuch as they would vary with the site and storm situations. It can be presumed that the runoff would contain traces of oils and phenols characteristic of runoff from railroad yards, plus trace levels of suspended solids and reduced sulfur, characteristic of coal pile drainage. The runoff from the process area would also qualify as contaminated runoff inasmuch as it would be expected to contain trace concentrations of byproduct chemicals such as phenols, ammonia and oils.

Drainage from the coal pile is another source of storm-generated wastewater. A distinguishing feature of

---

*Dr. Parsons is Director, Corporate Environmental Control; Mr. Ashworth is Assistant Director, Alternate Fuels Development, Arthur G. McKee and Company, Cleveland, Ohio.

Preceding page blank

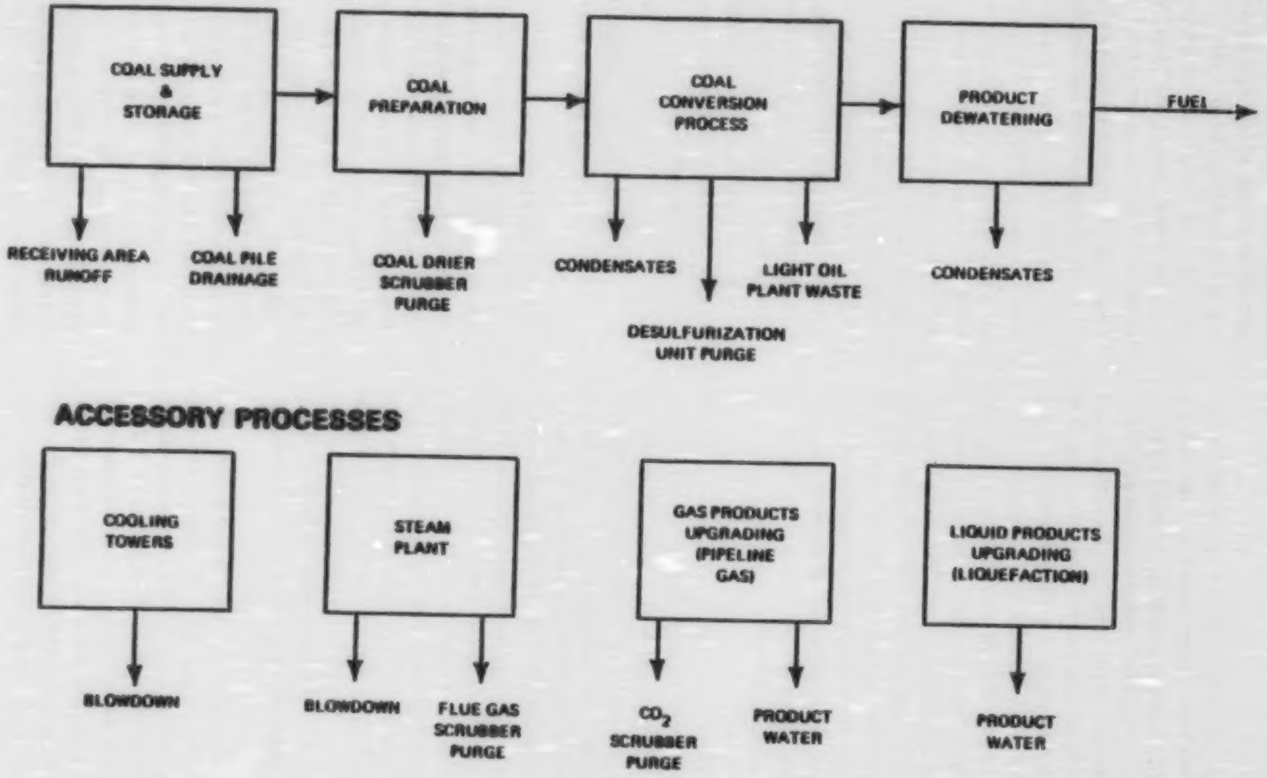

COAL SUPPLY & STORAGE
COAL PREPARATION
COAL CONVERSION PROCESS
PRODUCT DEWATERING
FUEL
RECEIVING AREA RUNOFF
COAL PILE DRAINAGE
COAL DRIER SCRUBBER PURGE
CONDENSATES
DESULFURIZATION UNIT PURGE
LIGHT OIL PLANT WASTE
CONDENSATES
ACCESSORY PROCESSES
COOLING TOWERS
STEAM PLANT
GAS PRODUCTS UPGRADING (PIPELINE GAS)
LIQUID PRODUCTS UPGRADING (LIQUEFACTION)
BLOWDOWN
BLOWDOWN
FLUE GAS SCRUBBER PURGE
CO2 SCRUBBER PURGE
PRODUCT WATER
PRODUCT WATER

Figure 1. Mainstream process schematic.

coal pile drainage is that it may be expected to contain substantial concentrations of pollutants. The grab sample analysis given in table 1 by C. W. Rice (ref. 1) suggests that coal pile drainage differs from coal washery waste in that concentrations of dissolved solids are high relative to concentrations of suspended solids.

The wastewater control significance of contaminated runoff becomes very great when regulations are based upon extreme value storm probabilities such as the 24-hour storm with a recurrence interval of 10 years. In their analysis of a 14,250 TPD Synthane Process plant, Kalfadelis and Magee (ref. 2) estimated design flows for coal pile drainage, process area runoff, and yard runoff as 5,000 gpm, 15,000 gpm, and 60,000 gpm respectively. If 5 inches of precipitation are taken as the representative storm for the Eastern coal fields, it can be projected that the volume requirement for containment of the runoff from the subject plant would amount to about 42 million gallons. The areal requirement would be about 20 acres. Storage requirements for Western coal fields would be less inasmuch as the 10-year, 24-hour storm would be expected to be in the range of from 1 to 2.5 inches.

Process Wastewater

The process wastes from coal conversion plants as illustrated by figure 2 are process specific in respect to volume and characteristics. Thus, the wastewater characteristics listed in table 1 should be considered as more illustrative than applicable. However, the condensate from the primary scrubber can be recognized as being of particular significance since it is a major flow that contains substantial concentrations of ammonium salts of chlorine and sulfur. The primary scrubber condensate also contains free ammonia, phenol, and cyanide compounds. Other condensates may contain volatile pollutants such as ammonia, phenol, or sulfur compounds, but are low in concentration of salts which improves the prospects for practical reuse after treatment. Purge flows from desulfurization, light oil refining, or product upgrading may contain high salt concentrations and, therefore, tend to possess limited prospects for reuse after treatment.

CONTROL ALTERNATIVES

Storm-Generated Wastewater

Wastewater control measures for stormwater commence with positive exclusion of uncontaminated runoff from contaminated runoff in order to minimize handling and storage problems associated with the vast flows. If minimum treatment is required, e.g., removal of traces of oil film, full flow devices similar to hay filters may be more feasible than storage concepts. If more sophisticated treatment is required—such as removal of suspended solids or phenol, control concepts providing for storage in conjunction with treatment will normally be employed out of consideration of process kinetic factors. Units such as variable level aerated ponds can be used for lowering trace levels of deoxygenating pollutants and suspended solids. The maintenance of culture activity during dry periods is a potential problem. In the case of concentrated flows such as coal pile drainage, sealed collection and storage facilities may be required to limit percolation. Underdraining of sealed areas has been advocated by some parties to verify the integrity of sealing procedures.

Process Wastewater

Wastewater control for process flows illustrated in figure 2 commences with at-the-source separation of oils and tars for separate collection and handling. Segregation of process wastes for recovery of ammonia and sulfur byproducts is common practice. Segregation of wastes is indicated for recovery of phenol, but segregation is unnecessary for destruction of phenol by biological or other means.

Reuse of wastewater flows is a universal objective of designers of modern process plants. In coal conversion processes, secondary condensates and other flows containing low concentrations of salts are readily amenable to incorporation into common reuse concepts. Parenthetically, primary scrubber condensate and other wastes purged from processes because of accumulations of salts or incompatible constituents are not readily amenable to incorporation into common recycle concepts. Primary scrubber condensate is the dominant salt bearing process waste and controls the characteristics of the effluent from the ammonia stripping operation. The effluent is corrosive. Recycle systems at byproduct coke plants have experienced pitting of 316 stainless steel; fiber reinforced plastic is a preferable material for low temperature service. Materials screening tests led to the use of Inconel water chambers and titanium tubes in a demonstration plant evaporator (ref. 4). Simplistic assignment of the effluent to recycle could result in significant revisions to materials specifications for high pressure service. The effluent from a lime still stripping operation will be saturated with calcium-sulfur compounds and will possess scale-forming tendencies upon subsequent chemical or biochemical oxidation of reduced sulfur to sulfate. Hence recycle alternatives are unattractive, and dilution below potential saturation is indicated in order to maintain viable treatment operations. Decreased biomass activity in the activated sludge process has been attributed to precipitation of calcium sulfate upon bio-oxidation of reduced sulfur.

Sulfur removal immediately following primary

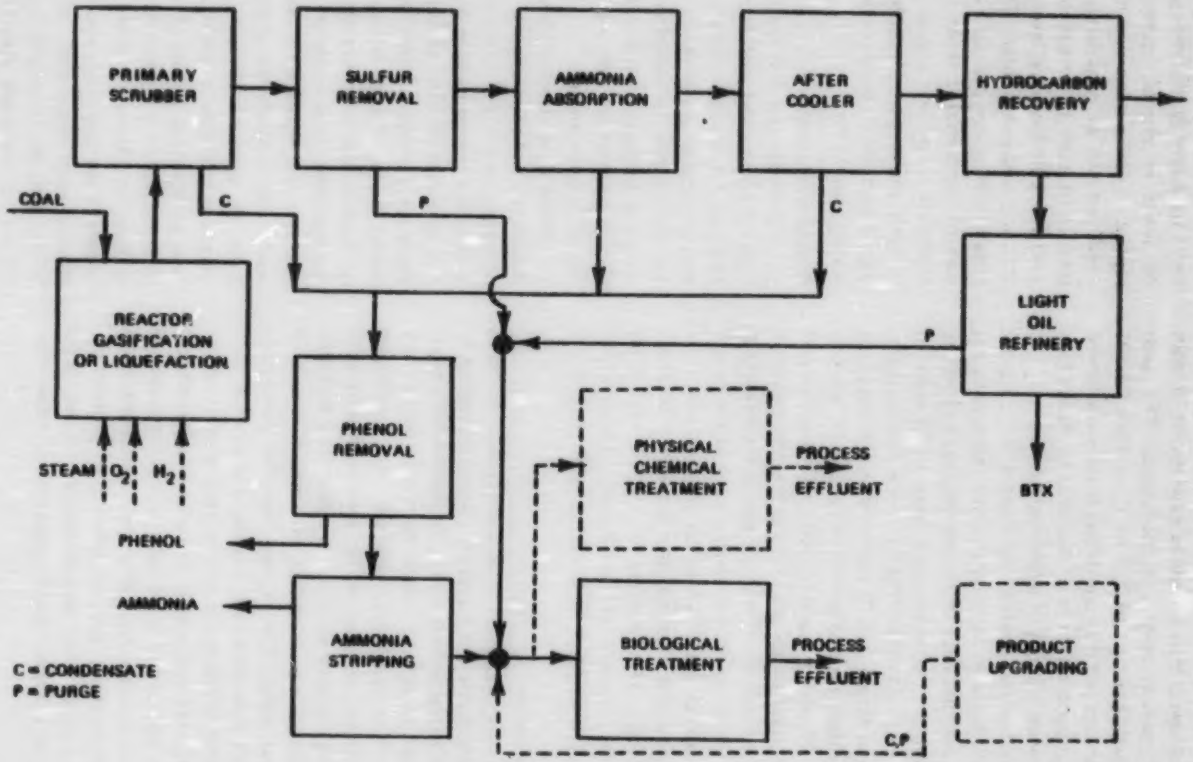

PRIMARY SCRUBBER
SULFUR REMOVAL
AMMONIA ABSORPTION
AFTER COOLER
HYDROCARBON RECOVERY
COAL
C
P
C
LIGHT OIL REFINERY
P
REACTOR GASIFICATION OR LIQUEFACTION
STEAM
O_2
H_2
PHENOL REMOVAL
PHYSICAL CHEMICAL TREATMENT
PROCESS EFFLUENT
BTX
PHENOL
AMMONIA
AMMONIA STRIPPING
BIOLOGICAL TREATMENT
PROCESS EFFLUENT
PRODUCT UPGRADING
C,P
C = CONDENSATE
P = PURGE

Figure 2. Coal conversion process effluents.

Table 1. Illustrative coal conversion process wastewater characteristics

	Coal Pile Drainage (ref 1)	Synthane Condensate *(ref 3)
Flow gal/ton	-	200
pH	7.6	9
Suspended Solids, mg/l	412	50
Dissolved Solids, mg/l	1413	-
COD, mg/l	1995	-
Cyanide, mg/l	3.2	0.4
Phenol, mg/l	-	3000
Chloride, mg/l	-	500
Ammonia, mg/l	-	8500
Sulfur, total, mg/l	-	500
Thiocyanate, mg/l	-	90

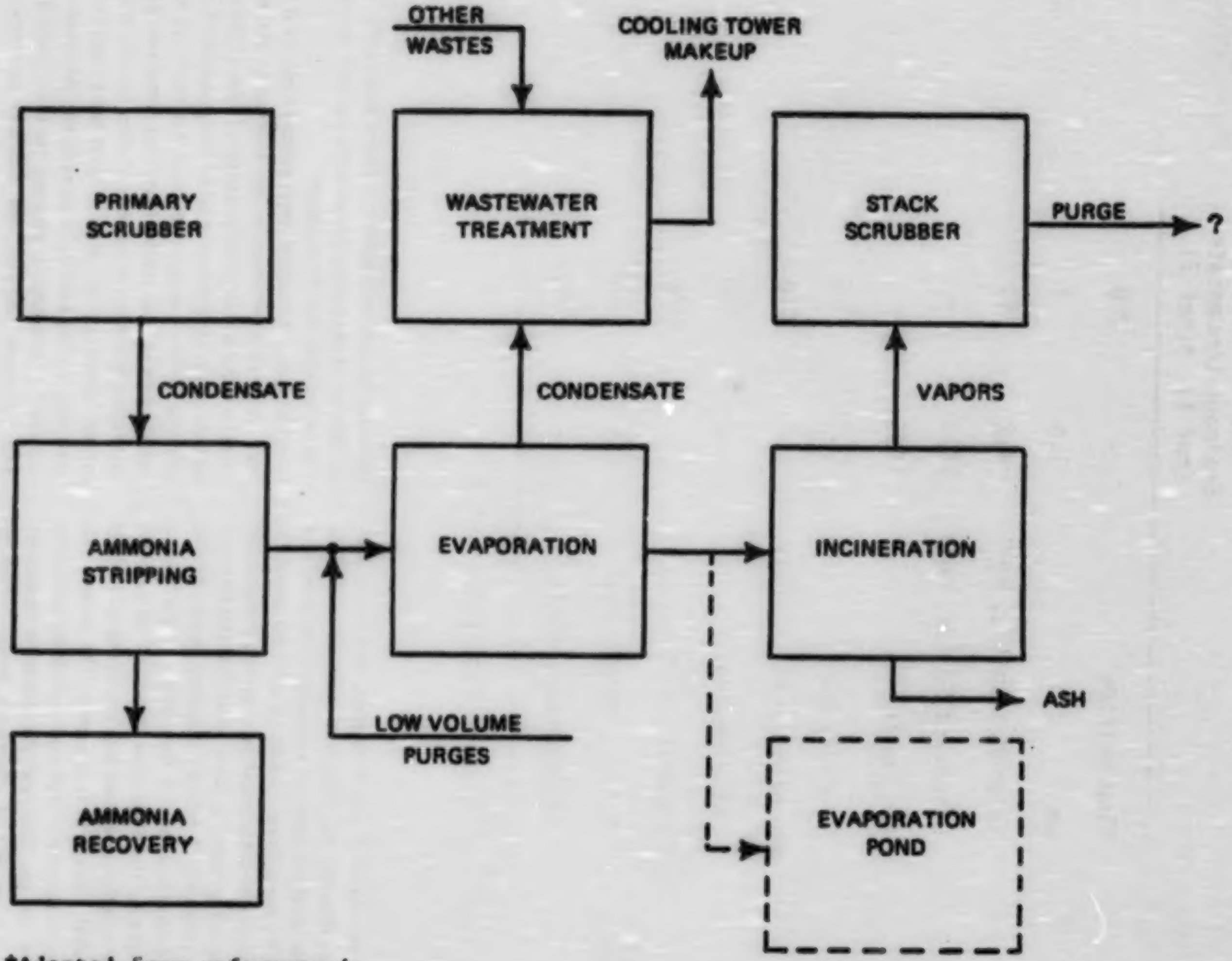
*Adapted from reference 3.

scrubbing per figure 2, where feasible, presents a conceptual opportunity for increased reuse of secondary condensates upon provision of independent recovery and treatment systems. Caustic could be used for ammonia stripping since low doses would be required. The stripper bottoms could be used for dilution of lime still bottoms from the stripping of primary scrubber condensate to enable biological treatment or for makeup to the flue gas scrubber system. The Sulfammon process is an example of a desulfurization operation that can be placed early in an applicable process flow sequence. The process features selective removal of hydrogen sulfide by controlled contact of the gas flow and the ammonia absorption solution. It is capable of effective hydrogen sulfide removal and the purge is compatible with biological treatment operations. Independent recovery and treatment of secondary condensates offers potential for improved wastewater control, but the practicality is limited by the increased cost of independent systems and by the limited volume of secondary condensates available for reuse.

Treatment-Oriented Alternatives

Biological treatment, physical-chemical treatment, and evaporation/incineration are alternatives for wastewater control by terminal treatment. None of the alternatives offers demonstrated technology capable of meeting new source standards for discharge from byproduct coke plants or presumably from coal conversion plants. Biological treatment is capable of effective removal of a broad spectrum of organic pollutants (particularly phenols) and reduced sulfur compounds. Although some removal of ammonia is effected by both volatilization and metabolic synthesis, the indicated performance is generally poor because of release of ammonia upon degradation of thiocyanates and amines.

Physical-chemical treatment uses activated carbon for adsorption of phenol. Additional unit processes are


OTHER WASTES
COOLING TOWER MAKEUP
PRIMARY SCRUBBER
WASTEWATER TREATMENT
STACK SCRUBBER
PURGE
?
CONDENSATE
CONDENSATE
VAPORS
AMMONIA STRIPPING
EVAPORATION
INCINERATION
ASH
LOW VOLUME PURGES
AMMONIA RECOVERY
EVAPORATION POND

*Adapted from reference 4.

Figure 3. WAL process (modified)*

required for the removal of cyanides, residual ammonia and reduced sulfur compounds. A physical-chemical system is being installed at a byproduct coke plant that employs adsorption of phenol by activated carbon in conjunction with pickle liquor coagulation (ref. 5). Development studies have been made relative to upgrading the removal of cyanides and ammonia by ion exchange.

A wastewater control demonstration plant incorporating evaporation and incineration of ammonia still waste has been installed (ref. 4). The process concept is outlined by the modified flow schematic given as figure 3. The concept of evaporation of ammonia still waste with disposal of dry ash facilitates the engineering of increased water reuse into coal conversion plants. However, the demonstration plant has not to date compiled a record of sustained performance that would qualify for status as demonstrated technology.

Summary and Conclusions

Wastewater control is a factor of prime significance in the siting, engineering, and operation of major coal conversion plants because of water supply constraints and stringent effluent standards. The sources of wastewater can be classified as stormwater generated and process generated. Pollutants associated with the wastes include phenols, ammonia, oils, cyanides, reduced sulfur compounds, and suspended solids. The stormwater wastes are indicated to consist of dilute, high volume flows from contaminated yard areas and more concentrated coal storage drainage. The process wastes are indicated to consist of wastes requiring blowdown such as salt bearing primary condensate and purges from unit processes plus wastes with low salt content that are more amenable to reuse.

A potential exists for corrosion and scale problems upon reuse of salt bearing primary condensates and purges from unit processes. The internal control of such problems in modern high-pressure coal conversion systems is viewed as particularly challenging and possibly beyond practical attainability. Therefore, segregation and terminal treatment of the wastes is advocated. Sulfur removal immediately following primary scrubbing offers a conceptual opportunity for increased recycle of secondary condensates. Such procedure should increase the practicality of reuse of low salt process wastes and collected stormwater waste after such reconditioning as required.

Alternatives for terminal treatment or reconditioning include biological, physical–chemical and evaporation–incineration. Biological treatment is developed to the extent that it has been employed at a number of coal carbonization plants for treatment of similar wastes, but the expected performance is inadequate to meet new source standards. Additional development is required to define the expected performance reliability and costs of physical–chemical and evaporation–incineration processes.

REFERENCES

1. Cyrus Wm. Rice Division, NUS Corporation, "Draft Development Document Iron and Steel Industry, Phase II," Addendum (August 1974). U.S. Environmental Protection Agency, Washington, D.C.
2. C. D. Kalfadelis and E. M. Magee, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes – Gasification, Section I: Synthane Process," EPA-650/2-74-009-b (June 1974). Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C.
3. A. J. Forney et al., "Analyses of Tars, Chars, Gases and Water found in Effluents from the Synthane Process," U.S. Bureau of Mines TPR 76 (January 1974).
4. R. Jablin and G. P. Chanko, "A New Process for Total Treatment of Coke Plant Waste Liquor," *Water 1973*, No. 136, Vol. 70 (1974), AIChE Symposium Series.
5. C. A. Naso and J. W. Schroeder, "A New Method of Treating Coke Plant Waste Waters," *AIME Ironmaking Proceedings*, Vol. 33 (1974).

A TAPERED FLUIDIZED-BED BIOREACTOR FOR TREATMENT OF AQUEOUS EFFLUENTS FROM COAL CONVERSION PROCESSES

Charles D. Scott, Charles W. Hancher,
David W. Holladay, and George B. Dinsmore*

Abstract

A bioreactor system based on a tapered fluidized bed is under development for the microbiological degradation of hazardous organic compounds expected in aqueous effluent waste streams from coal conversion processes. The concept will be used with fluidized particles having adhering microorganisms. The use of a fluidized reaction medium alleviates operational problems associated with biomass buildup and allows easy removal or addition of the active materials. The tapered reactor tends to stabilize the fluidized bed while allowing a much wider range of operating conditions. Preliminary experimental results from a study made with a 3-in. diameter tapered fluidized-bed reactor that contained adhering Pseudomonas *bacteria and operated aerobically indicate that the phenol content of a feed stream can be reduced to less than 25 ppb. This concept is compatible with multistage operation, and scale-up is considered practical.*

INTRODUCTION

The waste process and condensate liquors from coal gasification, liquefaction, or carbonization processes are qualitatively similar on a chemical constituent basis. They are expected to contain relatively large amounts of dissolved hydrogen sulfide and ammonia, as well as various phenols, thiocyanates, and lesser amounts of other hydrocarbons (refs. 1-4).

Some of the components of the waste stream may be present in sufficiently high concentrations to be recoverable. These may include H_2S, ammonia, and phenol. Both ammonia and H_2S could be recovered by stripping processes, while phenol recovery could be achieved by solvent extraction (ref. 5) (figure 1). However, phenol levels in the dephenolated liquors may still be greater than 50 ppm, well above the acceptable concentration for wastewater, and additional treatment will be necessary.

Studies of bacterial treatment of both raw and dephenolated waste liquors from gasification and carbonization processes have been made (refs. 4,6). In general, activated sludge systems utilizing large, stirred-tank reactors were used. Although residence times of many hours were required, very low phenol levels were achieved. To a lesser degree, thiocyanate levels were also reduced by the activated sludge system as were other organic compounds. Thus the processing scheme for coal conversion wastewater treatment will likely include a step for the biological degradation of phenols and other organic compounds. Since allowable phenol levels will probably be the controlling factor, the process step must be highly efficient in removing phenol. Further, although large stirred-tank reactors have been shown to operate in this application, efficient fixed- or fluidized-bed systems may be more compatible with the process needs. A tapered fluidized-bed bioreactor is being evaluated specifically for this application.

BIOLOGICAL DEGRADATION

The biological degradation of phenolic-type compounds has been extensively studied and can be represented by the overall reaction

$$\begin{gathered}\text{Substrate (phenol, etc.)} + \\ O_2 \xrightarrow[\text{microorganism}]{} CO_2 + \\ \text{increased biomass} + \text{reduced substrate.}\end{gathered} \qquad (1)$$

In this respect, the microorganism can be represented as a catalyst for the degradation. Actually, the degradation process is a relatively complex chemical pathway requiring a whole series of enzymes to catalyze the various degradation steps. The proper microorganism will contain all of the necessary enzymes to achieve a rather complete breakdown. Various types of *Pseudomonas* bacteria appear to be best adapted for phenol degradation. An excellent example of such a metabolic pathway was determined for *Pseudomonas putida* (ref. 7) (figure 2).

Biological systems using microorganisms in activated sludge processes have been used for treating aqueous waste containing organic compounds similar to those expected in coal conversion processes (refs. 4,6). When

---

*The authors are staff members of Oak Ridge National Laboratory, which is operated by Union Carbide Corporation for the U.S. Energy Research and Development Administration, and is located at Oak Ridge, Tennessee 37830.

Preceding page blank

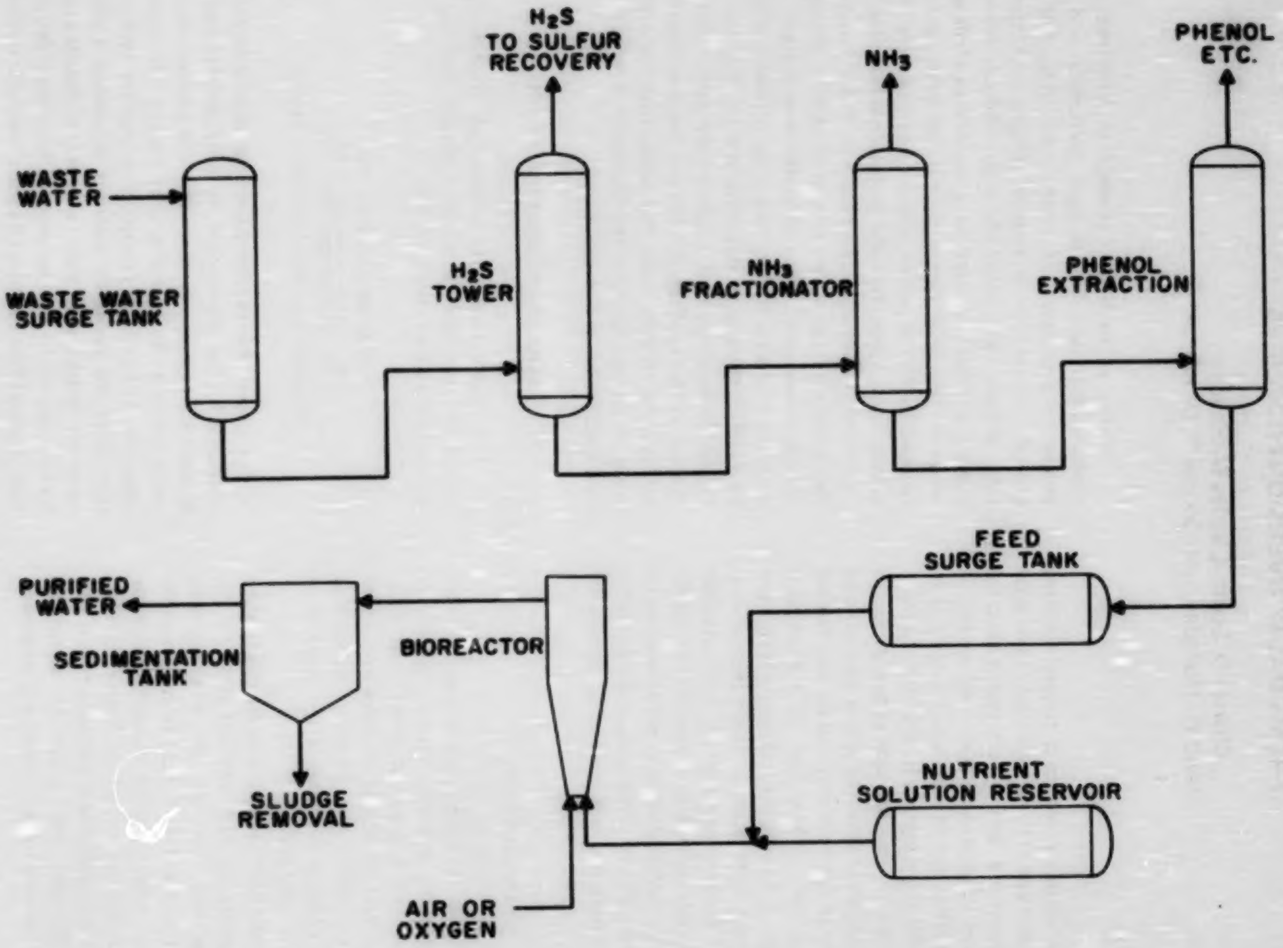

WASTE WATER
WASTE WATER SURGE TANK
H_2S TO SULFUR RECOVERY
H_2S TOWER
NH_3
NH_3 FRACTIONATOR
PHENOL ETC.
PHENOL EXTRACTION
FEED SURGE TANK
NUTRIENT SOLUTION RESERVOIR
BIOREACTOR
AIR OR OXYGEN
SEDIMENTATION TANK
PURIFIED WATER
SLUDGE REMOVAL

Figure 1. Possible simplified aqueous waste treatment flowsheet.

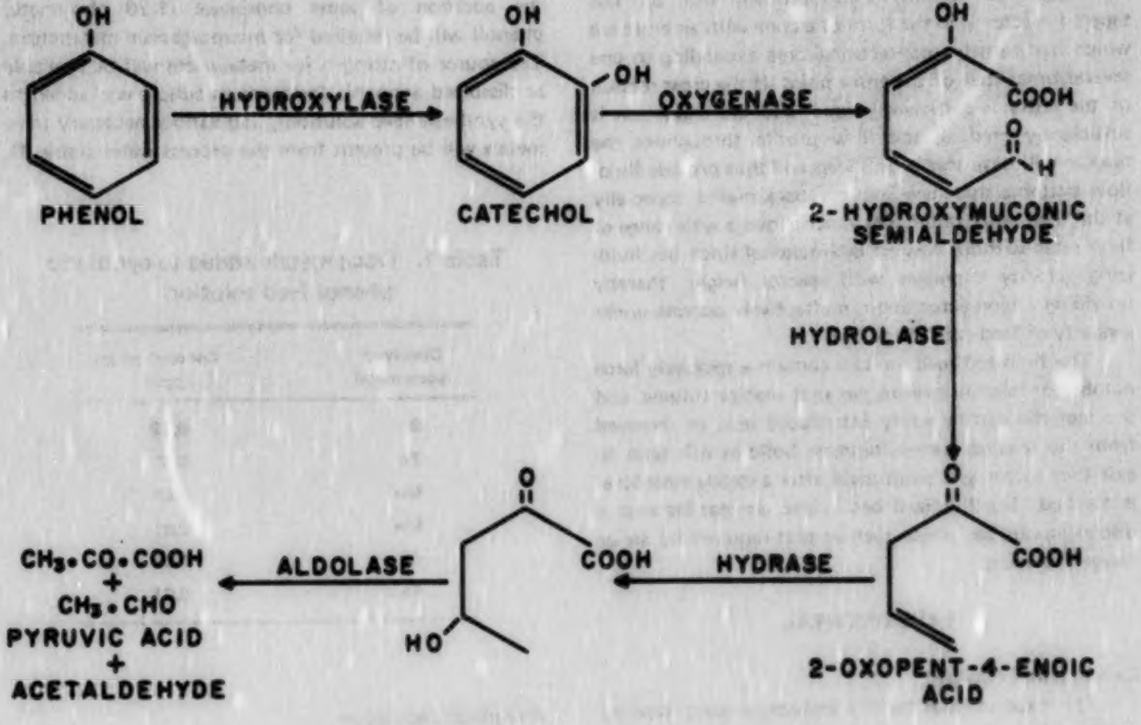


Figure 2. Simplified metabolic pathway used by *Psuedomonas Putida* to degrade phenol. (From ref. 7).

used with mixed cultures of microorganisms, these systems have been shown to reduce phenol levels from greater than 1000 ppm to less than 60 ppb, although residence times of many hours and very large reaction tanks were required (ref. 6). A mutant strain of *Pseudomonas* bacteria has now been developed commercially for the degradation of dissolved carbonaceous materials. This material, called Phenobac,* is reported to be highly efficient for phenol degradation. The biological process requires oxygen, which is best supplied by air or by simply adding O_2.

TAPERED FLUIDIZED-BED REACTOR CONCEPT

The usual activated sludge bioreactor utilizes a very large tank or pond in which most of the reactive microorganisms are maintained in dilute suspension by agitators or gas sparging. Such systems operate as single-stage batch reactors. Since the concentration of the pollutant in the effluent of such a reactor is the same as that in the reactor (both very low), the concentration driving force for the degradation reaction is very low. Thus, extremely large reactor volumes are required.

Many microorganisms can remain stable and viable while being attached to solid surfaces. The immobilized microorganisms can be used in columnar stagewise bioreactor configurations using fixed beds or fluidized beds and thus provide a much more efficient system. In the fluidized-bed concept, the fluidized particles will have adhering microorganisms and the aqueous waste stream will be the fluidizing medium.

The usual fluidized-bed has a relatively narrow range of optimum operating conditions. It is difficult to maintain nonfluctuating operation at optimum conditions since high bed expansion and low stability are frequently experienced. A new tapered reactor design is being investigated to circumvent this problem (ref. 8). The tapered reactor is in the form of a cone with an entrance which has a small cross-sectional area expanding to one several times that of the entry point. If the cross section of the entry is sufficiently small and the expansion is sufficiently gradual, the flow profile throughout the reactor will have few large eddies and thus provide fluid-flow patterns that have minimal backmixing, especially at the feed entry point. The taper allows a wide range of flow rates without loss of bed material since the fluidizing velocity decreases with reactor height, thereby providing a bioreactor that can effectively operate under a variety of feed conditions.

---

*Worne Biochemical, Inc., Frontage Industrial Park, Westville, New Jersey.

The fluidized medium can contain a relatively large number of microorganisms per unit reactor volume, and the material can be easily introduced into or removed from the reactor. Excess biomass buildup will tend to exit the reactor as a suspension after a steady-state level is reached. The fluidized bed is also compatible with a discontinuous gas phase such as that required by air or oxygen sparging.

EXPERIMENTAL

Experimental Facility

The experimental facility includes a glass, tapered fluidized bed, the diameter of which increases from 1 in. at the bottom of the reactor to 3 in. at the top in a 42-in. length (figure 3). Other equipment includes a feed reservoir, a feed metering pump, a settling chamber, and a waste reservoir. A pump is also available for recycling part of the waste stream for additional fluidization when needed. Since this is an aerobic bioprocess, provisions are available for introducing O_2 or air to the bottom of the column or to a feed stream oxygenator.

Materials

The solid particles used in the fluidized bed were anthracite coal in the particle size range of 0.0149 to 0.0177 cm. Although various microorganisms were used, including mixed cultures from activated sludge systems, the best results (and the experimental results reported here) were obtained from work with the mutant strain of *Pseudomonas* bacteria available under the trade name Phenobac.

Some scrub solutions from coal pyrolysis and hydrocarbonization were used in this study. The most definitive results, however, were obtained with synthetic feed solutions made from deionized water and reagent grades of phenol and other additives. It is anticipated that the pH of the coal conversion scrub solution may require adjustment to 6.5-8.0 via the addition of lime ($CaCl_2$ was added to the synthetic feed solution); also, the addition of some phosphate (1:70 phosphate: phenol) will be required for microorganism metabolism. The source of nitrogen for metabolism will be available as dissolved ammonia (ammonium sulfate was added to the synthetic feed solution), and various necessary trace metals will be present from the process water (table 1).

Table 1. Trace metals added to synthetic phenol feed solution

Dissolved trace metal	Concentration, ppm
B	0.02
Zn	0.01
Mo	0.01
Mn	0.01
Cu	0.01
Fe	0.01

Analytical Technique

Phenol analyses were carried out using previously developed procedures (ref. 9). Phenol concentrations as low as 1 ppm were determined by using the 4-aminoantipyrine colorimetric method, while levels of phenol down to 25 ppb were determined by steam distillation followed by extraction with chloroform and colorimetric analysis.

Operation

The reactor was operated with approximately 2 liters of an expanded fluidized bed of anthracite particles and approximately 0.5 liter of solution above the bed prior to the column exit. A relatively narrow range of inlet flow rates of 374 to 520 ml/min was used. The reactor operation was completely stable over this range, in fact, it was left unattended for a period of several days. In some tests, air or oxygen was introduced at the bottom entry point through a porous metal frit, resulting in a three-phase system. However, the most efficient operation was found when the feed solution was presaturated with oxygen and a third phase was not maintained in the reactor.

The microorganisms were introduced into the reactor by circulating a suspension of the live microorganisms through the reactor for 8 to 12 hr. This period was sufficient for establishing an initial "seed" of attached microorganism that then tended to multiply rapidly,

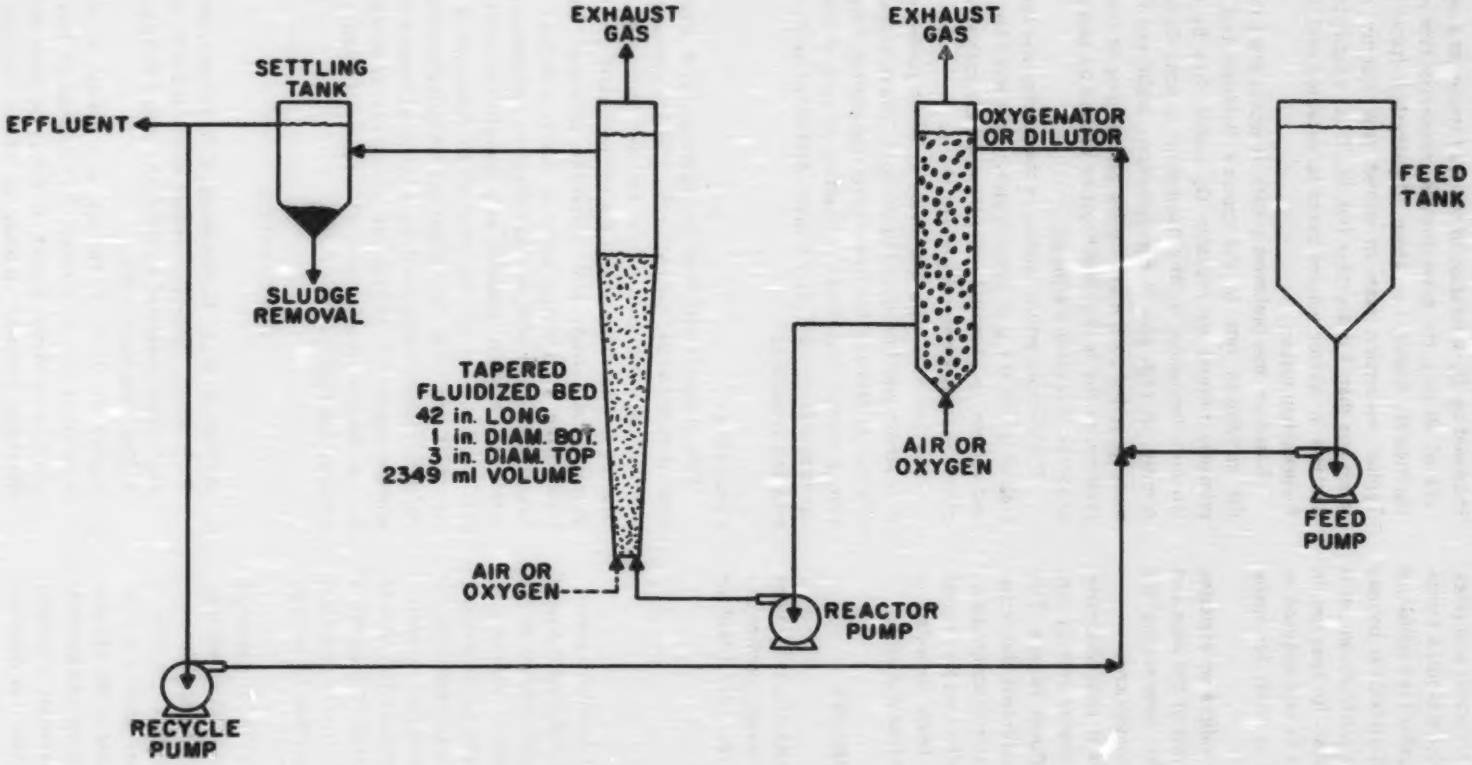

EXHAUST GAS
EXHAUST GAS
SETTLING TANK
EFFLUENT
OXYGENATOR OR DILUTOR
FEED TANK
SLUDGE REMOVAL
TAPERED FLUIDIZED BED
42 in. LONG
1 in. DIAM. BOT.
3 in. DIAM. TOP
2349 ml VOLUME
AIR OR OXYGEN
AIR OR OXYGEN
FEED PUMP
REACTOR PUMP
RECYCLE PUMP

Figure 3. Experimental tapered fluidized bed bioreactor system.

reaching a steady-state condition after about one week. This is the condition at which additional biomass formation results in aqueous suspension rather than additional attachment. At this point, the fluidized bed can be used for the continuous degradation of a waste stream, or it can be stored at 4°C almost indefinitely for later use. In the latter case, the bed material can be reintroduced to the bioreactor and the system will be ready for operation in a very short time.

Flow rates were measured by calibrated metering pumps and/or rotameters, and aliquots of the inlet and effluent streams were collected for determining the concentrations of phenol and other constituents.

A stock solution with a specific phenol concentration was used in most cases, and the phenol inlet concentration was varied by utilizing effluent recycle. This recycle mode of operation could represent the actual method to be used for very high phenol concentrations, or the lower inlet concentrations (after recycle mixing) could be indicative of the lower levels expected in instances where a phenol recovery process was used.

RESULTS AND CONCLUSIONS

The tapered fluidized-bed bioreactor is still in the bench-scale development phase. However, preliminary results indicate that the system will be a useful tool for degrading phenol to very low levels.

Experimental Results

Several scouting tests were made in which a preliminary feed stream containing 450 to 4,800 ppm phenol was continuously mixed with a recycle stream of the reactor effluent to make up the bioreactor feed stream. Oxygen was added either as a gas sparge (air or oxygen) to the bottom of the fluidized bed or by saturating the feed stream with oxygen prior to its entry to the reactor.

No attempt was made to evaluate the effect of feed stream flow rate. There was no evidence of fluid-phase mass transport control of the reaction. Since a single bed volume was used in these studies, the effect of bed size has not yet been established.

The system was found to be capable of degrading phenol to levels less than 25 ppb with reactor residence times as low as a few minutes. As the phenol inlet concentration was increased in each series of test runs, a breakthrough point was reached where additional inlet phenol resulted in a significant increase in the effluent phenol concentration. With air sparging or a feed stream saturated with oxygen at ambient pressure, a specific conversion rate of about 6.6 g/day·liter was observed (table 2). When the oxygen content of the system was increased by O_2 saturation of the feed stream at a pressure of 40 psig, the breakthrough conversion rate was significantly higher, i.e., about 10 g/day·liter (table 2). Typical conversion rates in stirred tank reactors are much less than 1 g/day·liter (ref. 6). Thus, a significant decrease in reactor volume could be expected with the fluidized-bed system.

Based on this preliminary data, it would seem that the conversion rate in the tapered fluidized bed is primarily limited by available O_2 rather than by an inherent limitation in the biological system. Consequently, at high phenol concentrations, additional O_2 must be added to the system by gas sparging or overpressure, or the feed stream must be diluted by recycle of some of the reactor effluent.

The microorganism loading in the reactor was very high at about 0.1 g of dried organisms per milliliter of bed volume, and biomass production was typically 0.6 g of dry microorganisms per gram of phenol.

Scouting tests were also made in which potassium thiocyanate was introduced in the feed. The bioreactor was not as efficient for thiocyanate degradation. However, a typical feed stream containing 34 ppm of thiocyanate was reduced to 11 ppm. Additional work is required in this area.

Conclusions

Preliminary results from the operation of a small, tapered fluidized-bed bioreactor for the degradation of dissolved phenolic compounds indicate that such a concept is potentially useful for the treatment of the aqueous waste from coal conversion processes. The reactor uses a multistage concept, which is at least a factor of 10 more efficient than the more conventional stirred-tank reactors, allowing very low effluent values. Additional studies will be required to determine the effects of bed height and other operating parameters, and long-term operation with an actual coal conversion aqueous waste will be required to confirm its utility. Scale-up by at least a factor of 10 in column diameter is probably practical.

REFERENCES

1. Johnson, C. A., M. C. Chervenak, E. S. Johnson, and R. H. Wolk, "Scale-Up Factors in the H-Sol Process," paper presented at the 65th Annual Meeting, AIChE, New York, 1972.
2. Forney, A. J., W. P. Haynes, S. J. Gasior, G. E. Johnson, and J. P. Strakey, Jr., "Analysis of Tars, Chars, and Water Found in Effluents from the Synthane Process," Bureau of Mines Technical Progress Report TRP 76, January 1974.

Table 2. Phenol degradation rates in tapered fluidized-bed bioreactor[a]

Feed stream[b]		Effluent phenol concentration,[c] ppm	Reactor conversion rate,[d] g/day-liter	Method of oxygenation
flow rate, ml/min	phenol concentration, ppm			
409	14	0.05	2.4	Air sparge in column
425	38	1	6.6	Air sparge in column
412	140	100	6.9	Air sparge in column
475	9	< 0.025	1.8	Feed stream saturated with O_2 at ambient pressure
480	17	.050	3.0	Feed stream saturated with O_2 at ambient pressure
482	20	.080	3.9	Feed stream saturated with O_2 at ambient pressure
500	36	1	6.6	Feed stream saturated with O_2 at ambient pressure
505	31	10	6.8	Feed stream saturated with O_2 at ambient pressure
374	30	< 0.025	4.6	Feed stream saturated with O_2 at 40 psig
388	56	< 0.050	9.3	Feed stream saturated with O_2 at 40 psig
391	63	0.50	10.2	Feed stream saturated with O_2 at 40 psig

[a] All runs were made at ambient pressure, 25 ± 2°C, pH 7.0.-7.2.

[b] In all tests recycle effluent was used with a primary feed stream containing 450 to 4800 ppm of phenol.

[c] Most sensitive assays of less than 1 ppm had a sensitivity of 0.025 ppm. The less sensitive assay had a sensitivity of 1 ppm.

[d] Included the volume of the fluidized bed, as well as the volume of solution above the bed and the volume of the settling chamber.

3. El Paso Natural Gas Company, "Second Supplement to Application of El Paso Gas Company for a Certificate of Public Convenience and Necessity," Docket No. EP73-131, October 1973.
4. Ashmore, A. G., J. R. Catchpole, and R. L. Cooper, "The Biological Treatment of Carbonization Effluents – I. Investigation into Treatment by the Activated Sludge Process," Water Research, 1:605, 1967.
5. Lauer, F. C., E. J. Littlewood, and J. S. Butler, "Solvent Extraction Process for Phenols Recovery from Coke Plant Aqueous Waste," *Iron and Steel Engineer Year Book*, p. 315, 1972.
6. Davis, W. R., "Control of Stream Pollution at the Bethlehem Plant," *Iron and Steel Engineer Year Book*, p. 785, 1972.
7. Sala-Trepat, J. M., K. Murray, and P. A. Williams, "The Metabolic Divergence in the Meta Cleavage of Catechols by *Pseudomonas Putida*," *Eur. J. Biochem.* *29*, 347 (1972).
8. Scott, C. D., C. W. Hancher, and S. E. Shumate, II, "A Tapered Fluidized Bed as a Bioreactor," presented at the 3rd International Conference on Enzyme Engineering at Reed College, Portland, Oregon, Aug. 3-8, 1975 (proceedings to be published by Plenum Press).
9. *Standard Methods for the Examination of Water and Wastewater*, 12th Ed., Am. Public Health Assoc., New York, 1965.

CLIMATIC EFFECTS ON WASTEWATER TREATMENT*

Stanley L. Klemetson, Ph.D.†

Abstract

The development of coal gasification process to produce synthetic natural gas (SNG) will create potential pollution problems. The sources of pollutants at the site and basic constituents of the waste streams are discussed. The wastewaters are generally treated in several typical physical, chemical, and biological treatment processes.

The principal factors of the climate—temperature, solar radiation, heating days, wind roses, precipitation, and snowfall, are discussed in their relationship to wastewater treatment processes. The effects of temperature variations on the biological reaction rates, BOD, removals, and detention time are presented. It was recommended that more concern be placed on the effect of climatic conditions on wastewater treatment design.

INTRODUCTION

There is an energy crisis in the United States. One solution to this problem is seen in the conversion of coal to a clean fuel by the use of a coal gasification process. A primary concern is that the treatment and/or conversion process that generates the clean fuel does not itself become a major pollution source. While the potential pollutants can be expressed in any or all of the three possible states of air emissions, solid wastes, and liquid effluents (figure 1), all of them ultimately contribute to the wastewater effluents of the plant and its site.

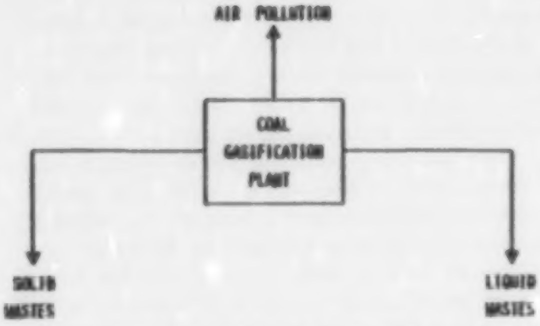


Figure 1. Potential states of pollutants.

Energy production utilizing a coal gasification process to produce high-Btu synthetic natural gas (SNG) with a heating value of about 970 Btu/SCF will become a reality in the United States within the next few years. The enactment of increasingly stringent environmental legislation requires that information be made available on the types of wastes to be generated, the environmental effects of these wastes, and the best available treatment technology. Since coal gasification plants are net consumers of water, it is also important to assess the wastes and the treatment methods from the standpoint of water reuse potential. The proposed plants will be operated under widely different climatic conditions, and this could have a significant effect on the choice of wastewater treatment processes. These aspects of control technology are summarized in table 1.

A variety of processes has been developed to produce both high-Btu and low-Btu synthetic natural gas (table 2). Each of the gasification processes has a different configuration of unit operations, but the resulting wastewater effluents are somewhat similar. Since the Lurgi gasification process is currently being planned for several areas in the Northern Great Plains, the discussion will be limited to this process. However, much of the information will be applicable to the other processes also. The purposes of this paper are presented in table 3.

GASIFICATION PROCESS

The Lurgi coal gasification plants planned for construction in the United States are being designed to produce 250 x 10^6 SCFD of medium to high Btu synthetic

Table 1. Control technology

- Types of wastes
- Environmental effects
- Available treatment technology
- Water reuse potentials
- Climatic effects on wastewater treatment

---

*This work was carried out as part of Grant No. ENG7510251 from the National Science Foundation, and as a Visiting Professor, Industrial Environmental Research Laboratory, EPA.

†Assistant Professor, Department of Civil Engineering North Dakota State University, Fargo, North Dakota.

Table 2. Typical coal gasification processes under development

High-Btu gasification	Low-Btu gasification
Bi-gas	Agglomerating gasifier
CoGas	AtGas
CO_2 acceptor	Entrained gasifier
HyGas	Koppers-Totzek
Lurgi	Lurgi
Molten salt	Stirred fixed bed
Synthane	

natural gas (SNG) that will yield about 970 Btu/SCF. The average consumption of coal in these plants is about 1,000 to 1,500 tons per hour, and the average annual usage of raw water is about 17,500 acre-feet (AF). The plants will be required to meet strict air, solid waste, and water pollution regulations, and will be expected to practice conservation by a reasonable water reuse program.

The complexity of the coal gasification process requires that the major operations and sources of effluents be described in terms of modules that will allow for the analysis of process streams and effluents. A simplified block diagram of the Lurgi gasification process and the related facilities is presented in figure 2. The various process and effluent streams have been left off since they are beyond the scope of this paper. The modules have been given a number and are described in more detail in table 4.

Table 3. Scope of paper

- Potential sources of wastewater effluents
- Typical constituents of wastewater streams
- Typical wastewater treatment processes
- Potential climatic effects
- Climatic effects on wastewater treatment

Several of the modules are affected directly by the climate. Rainfall runoff has a great potential as a source of pollution. Poor housekeeping in some areas of the plant in the winter can result in very high concentrations in the runoff during the spring thaw. Improper storage of ash piles and feed coal can result in leachate and runoff problems during spring thaw and rainstorms. All of the wastewater recovery and treatment processes produce some sludges, brines, or effluents that will cause pollution if not disposed of adequately. Temperature and other climatic effects will affect the quantities of these materials to be disposed of.

WASTEWATER CONSTITUENTS

There is a wide variety of products, byproducts, and waste effluents produced by a coal gasification plant. Many of these wastes are complex organics, some are very toxic and/or carcinogenic. The actual concentration of each constituent is dependent on the constituents in the feed coal and on the plant operation. Some of the typical constituents in the wastewaters that are determined before a treatment facility is designed are shown in table 5. This is not a complete list, but rather indicates some of the difficulties that might be encountered in the treatment process.

WASTEWATER TREATMENT PROCESSES

The complexity of the various waste streams from a gasification plant has led to a variety of research projects and contracts to determine the best and most economical processes for use. The enactment of stricter effluent standards for many types of pollution sources has put pressure on the designers of gasification plants to adequately dispose of their wastes. Some of the typical treatment processes suitable for use in a coal gasification plant are presented in table 6. Again this list is far from complete, but is representative of some of the treatment methods. Most of the treatment processes require that an adequate pretreatment has previously been used. Some of these processes are also used to produce clean water needed in various parts of the plant.

There are various paths that can be followed as far as the selection of treatment units that will produce comparable treatment results; however, the biological processes are often selected as part of the process since their overall costs are generally lower. For this reason, most of the effects of climatic conditions will be discussed with regard to the biological processes. There are

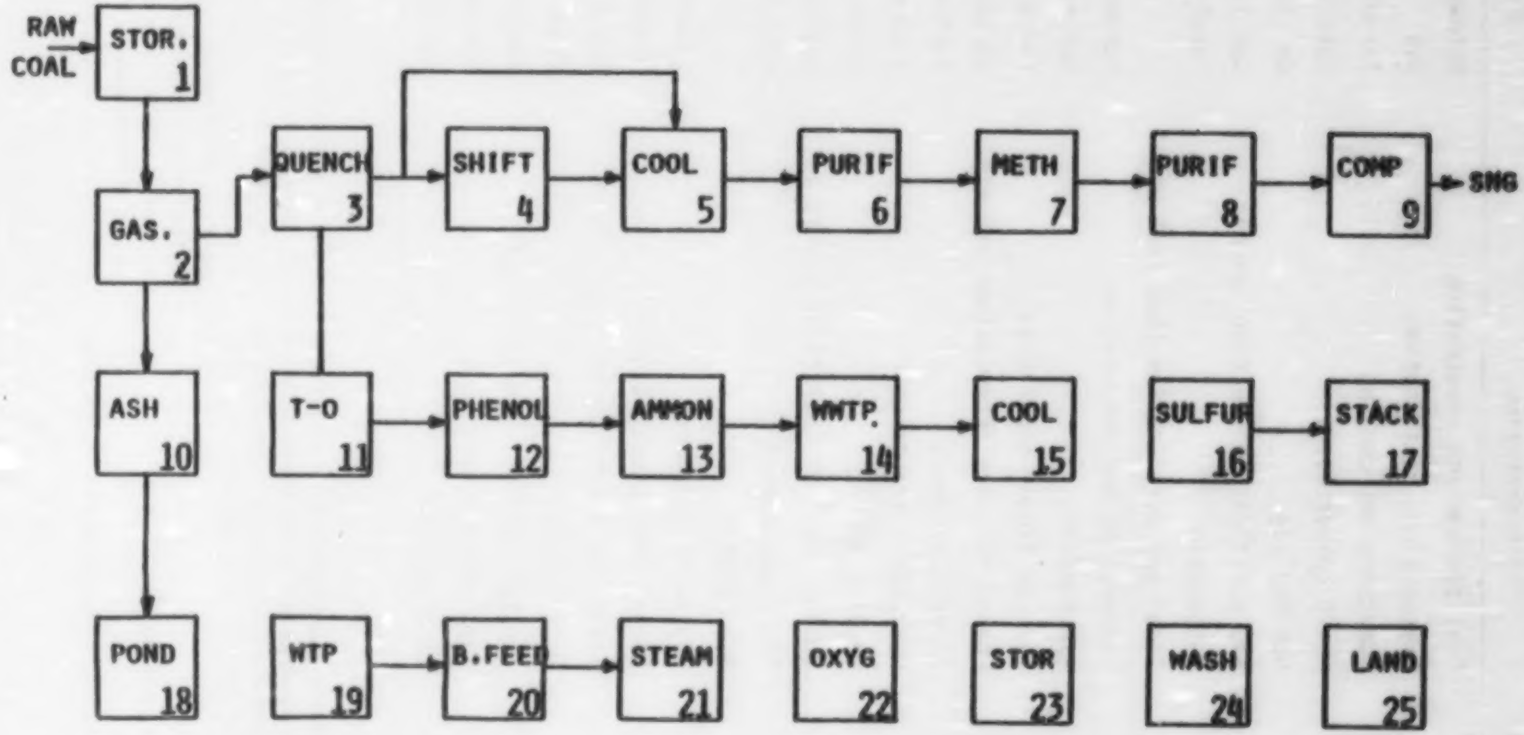

RAW COAL
STOR. 1
GAS. 2
QUENCH 3
SHIFT 4
COOL 5
PURIF 6
METH 7
PURIF 8
COMP 9
SNG
ASH 10
T-O 11
PHENOL 12
AMMON 13
WWTP. 14
COOL 15
SULFUR 16
STACK 17
POND 18
WTP 19
B.FEED 20
STEAM 21
OXYG 22
STOR 23
WASH 24
LAND 25

Figure 2. Potential sources of wastewater effluents at coal gasification plant.

Table 4. Effluent source modules of coal gasification plant

Module	Description	Effluent
1	Coal storage and preparation	Rainwater runoff
2	Oxygen blown gasification	Ash
3	Quenching and cooling	Tar-oil
4	Shift conversion	Catalyst
5	Gas cooling	Gas liquor
6	Gas purification (Rectisol wash)	Gas liquor
7	Methanation	Catalyst
8	Final gas purification (Rectisol wash)	
9	Compression and dehydration	Condensate
10	Ash handling	Wet ash
11	Tar-gas liquor separation	Tar & oil water
12	Phenol recovery (Phenosolvan process)	Wastewater
13	Ammonia recovery	Wastewater
14	Wastewater treatment	Sludge & effluent
15	Cooling tower	Blowdown
16	Sulfur recovery (Stretford process)	Wastewater
17	Stack gas cleaning	Wastewater
18	Ash ponds	Leachate & runoff
19	Raw water treatment	Sludge
20	Boiler feed preparation	Sludge & brine
21	Steam and power plants	Ash & blowdown
22	Oxygen plant	Condensate
23	Storage (product and byproduct)	Runoff
24	Washroom and work area	Sewage & runoff
25	Land surfaces	Runoff

also definite climatic effects in the physical and chemical processes. Any treatment process that is operated in the outside environment will be subjected to the effects of the climate that will affect their operation and maintenance.

CLIMATIC CONDITIONS

One of the principal climatic factors that affects the design of wastewater treatment facilities is temperature. The historical data (ref. 1) for temperatures at Dunn Center, North Dakota, are presented in figure 3. The wintertime average temperatures fall to -10° C with about one half of the year having temperatures below 0° C. The extremes range from -45° C to +45° C, and can cause severe effects on the operation of the treatment units or biological systems. The winter low temperatures are sustained for extended periods of time and will effec-

Table 5. Typical constituents of wastewater streams

Monovalent phenols
Multivalent phenols
NH_3 fixed (CL)
NH_3 fixed (fatty acids)
NH_3 free
Fatty acids
CL
F
NAOH
CO_2
H_2S
HCN
BOD_5

tively draw the available heat out of almost any process. The summertime highs combined with heat from the plant can also cause a detrimental effect on the operation of the units.

The amount of sunshine and the net solar radiation affects the rate heat transfer from cooling ponds and biological ponds. It affects the amount of photosynthesis in the ponds and, ultimately, the amount of oxygen available for biochemical oxidation of waste materials. A heat input of 0.2713 Btu/sf/day is produced by one Langleys/day. The historical data are presented in figure 4.

Atmospheric temperatures less than about 18° C are considered heating days. While this concept is not completely applicable to wastewater treatment processes, the curves in figure 5 are indicative of the relative cold and hot period in the area where the plant is to be built. These climatic conditions could be considered favorable from the standpoint of cooling of the process waste streams and the cooling water. The rate of cooling will affect the design of the holding ponds or units where the hot waste streams are allowed to cool some before being sent to the wastewater treatment processes.

The wind speed and direction at the site will affect the rates of cooling and the rate of oxygen transfer in ponds. The wind speed and atmospheric temperatures are combined to produce a wind chill factor that reaches very low temperatures. With an average wind speed of about 15 mph, it could be an important factor in the design of treatment methods. A typical wind rose is presented in figure 6.

One of the principal contributors to pollution is rainfall itself. Runoff from land surfaces in work and storage areas, as well as stockpiles, can contribute large quantities of pollution. The contamination of the aquifer from leachate is also a problem in some areas. The control of the waters produced by runoff is an important part of the wastewater treatment process. As shown in figure 7, the low precipitation in some parts of

Table 6. Typical wastewater treatment processes

Physical	Chemical	Biological
Sedimentation	Neutralization	Activated sludge
Flotation	pH adjustment	Trickling filter
Oil separation	Coagulation	Aerated lagoons
Stripping	Precipitation	Waste stabilization ponds
Solvent extraction	Oxidation	
Adsorption	Ion exchange	
Combustion		
Filtration		

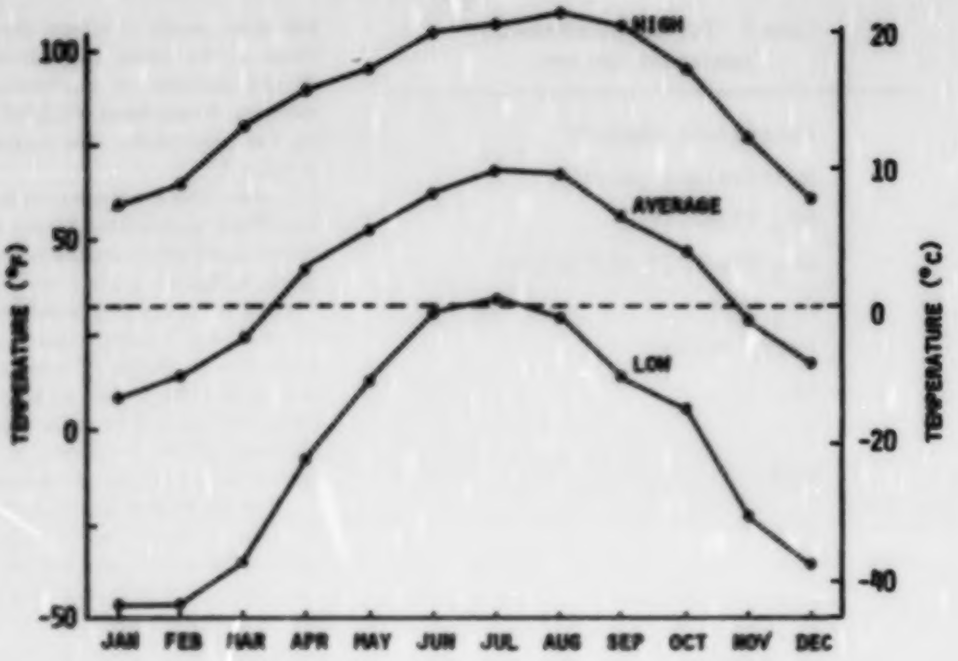


Figure 3. Monthly average and extreme air temperature, Dunn Center, North Dakota (ref. 1).

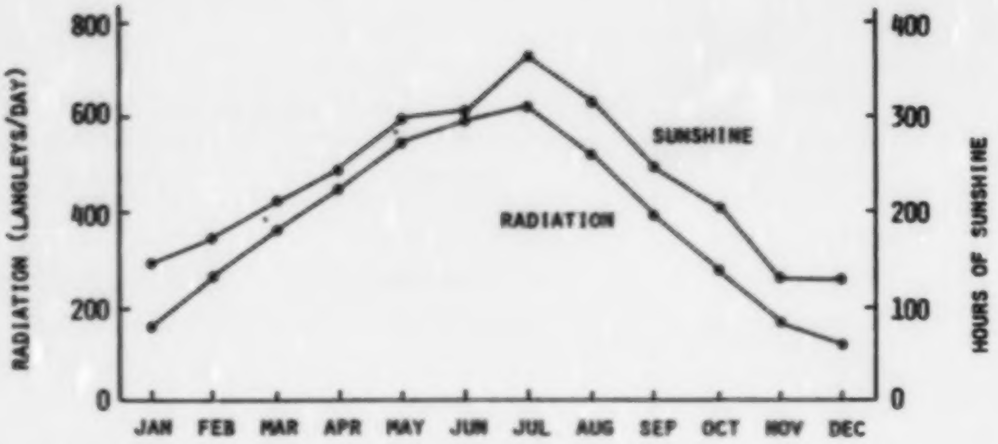


Figure 4. Estimated mean daily solar radiation and total hours of sunshine, Dunn County, North Dakota (ref. 1).

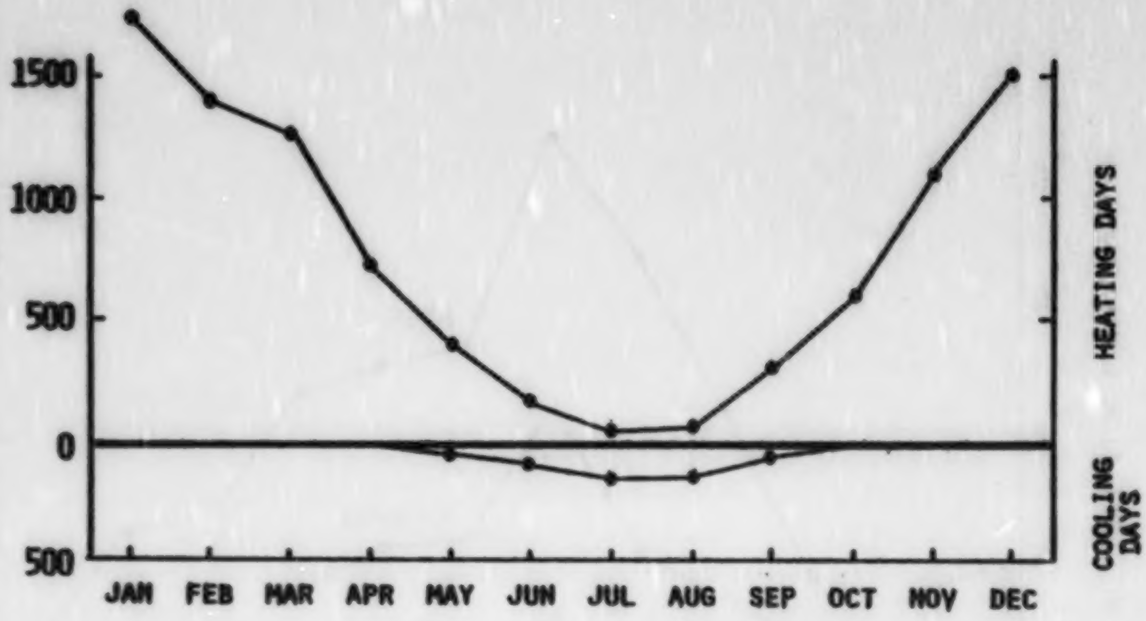


Figure 5. Heating and cooling degree days, Dunn Center, North Dakota (ref. 1).

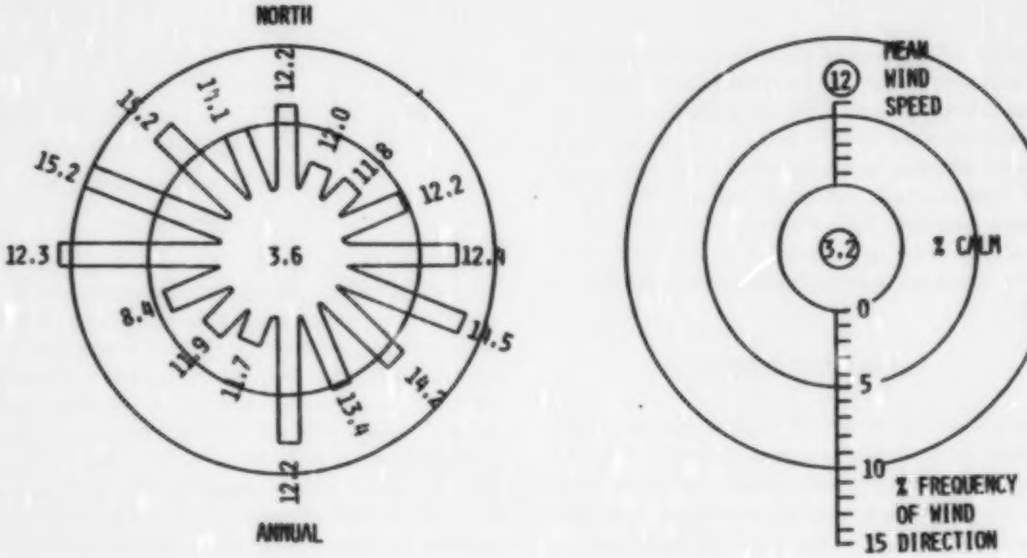


Figure 6. Percent frequency of wind direction and mean wind speeds, Dickinson, North Dakota, 1960-1971 (ref. 2).

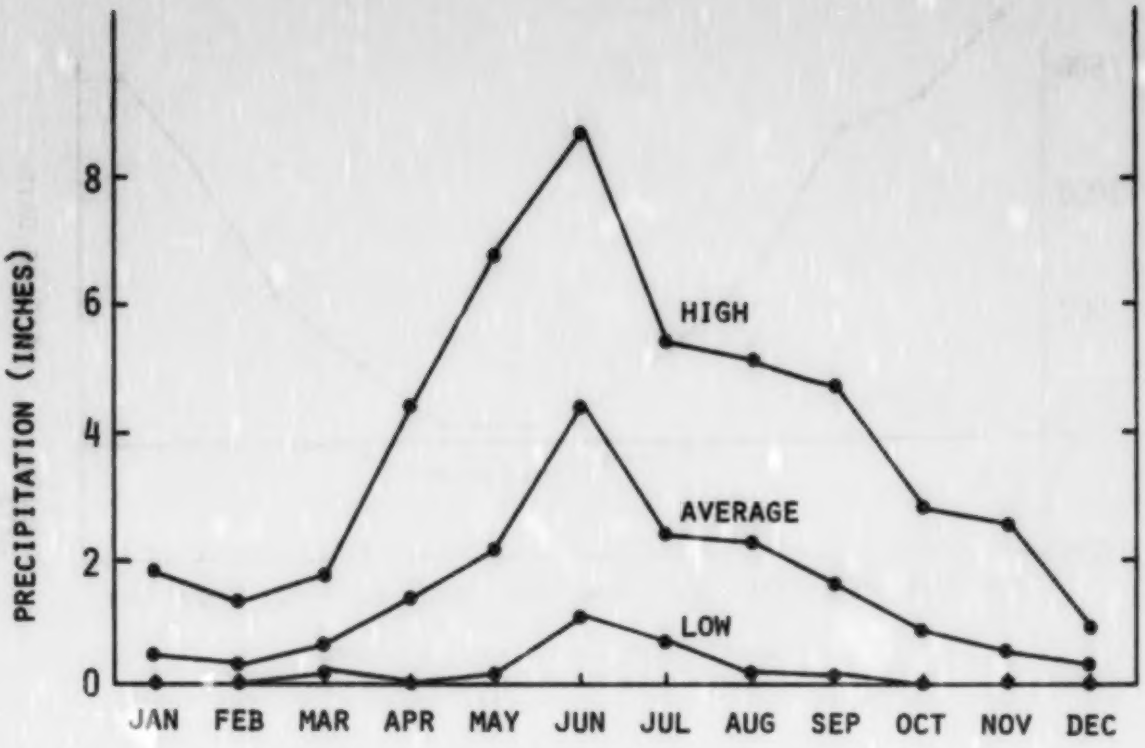


Figure 7. Monthly average and extreme precipitation,
Dunn Center, North Dakota (ref. 1).

the country will determine the degree of treatment required to conserve water and provide for water reuse.

Coal gasification plants located in northern climates are also confronted with snowfall and drifts. While actual snowfalls may be considered small in many cases, the drifts that build up may affect the operation of the wastewater treatment units. Generally, the snow is more of an inconvenience rather than a detriment to operation. The historical snowfall records are presented in figure 8.

CLIMATIC EFFECTS

There is a wide variety of possible climatic effects on wastewater treatment processes. Some of these are important and some are insignificant. A few of these effects on the biological treatment systems are presented in table 7. The variation of the rate of biological activity will be discussed first.

The biological reaction rate constant, k_1, varies with temperature according to the following equation:

$$k_t = k_1 \, \theta \, (t - 20)$$

where:

k_t = rate constant at desired temperature

k_1 = rate constant at 20° C

t = temperature, °C

Each type of biological or chemical process has a different value for the temperature coefficient, θ. This coefficient for several types of biological treatment processes is shown in table 8 (ref. 3). The equation is considered valid only within the indicated temperature ranges. A plot of a typical reaction rate versus temperature is shown in figure 9. This curve shows that the organisms are slowed down by the low temperatures, but are not always killed if maintained at that temperature for short periods of time. At the other end, however, temperatures above 45° C will usually kill the mesophilic bacteria normally found in these waters. Similar equations exist for the chemical process; however, the temperature coefficient and reaction rate constants will be

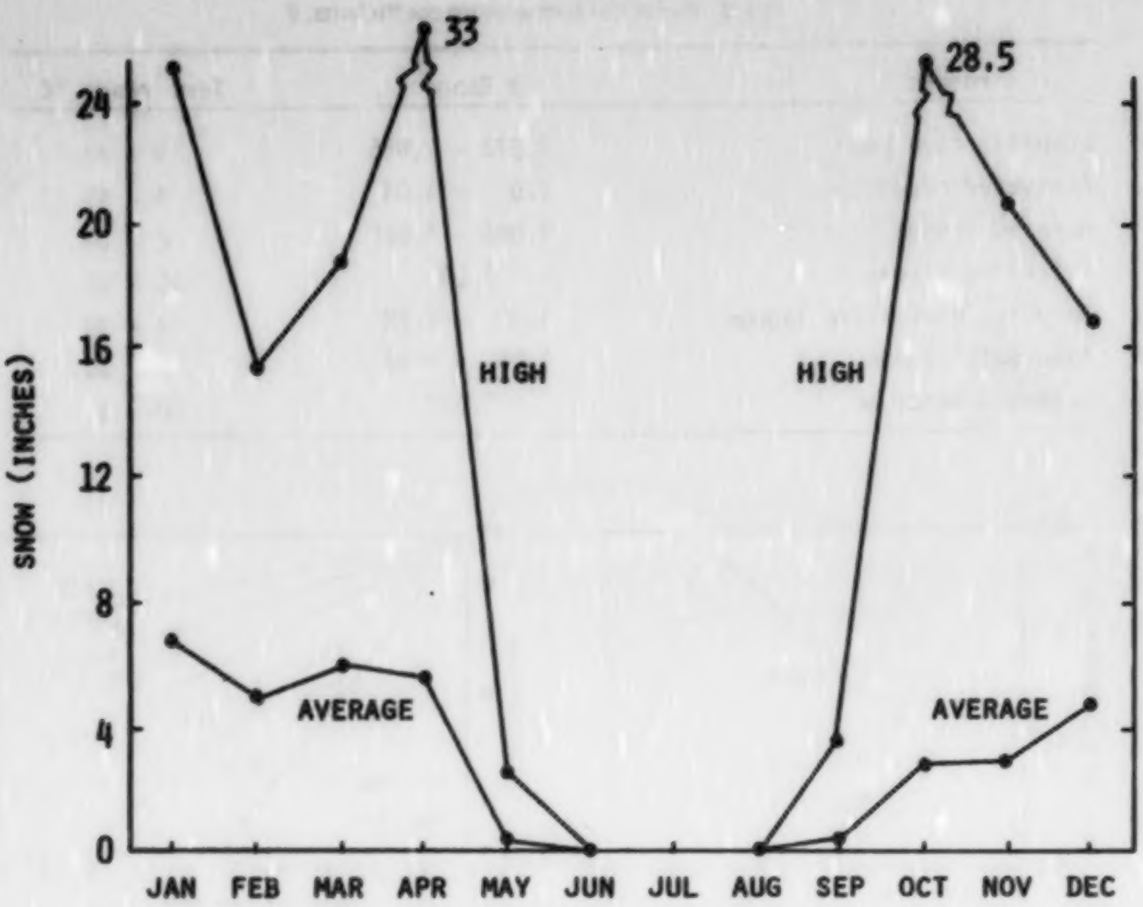


Figure 8. Monthly average and extreme snowfall, Dunn Center, North Dakota (ref. 1).

Table 7. Climatic effects on wastewater treatment

Variations in rate of biological activity
Atmospheric oxygen transfer rate
Changes in oxygen solubility
Variations in photosynthetic oxygen production
Variations in detention time
Variations in treatment efficiencies

different. Likewise, physical processes are affected by temperature variations.

One of the detrimental effects of low temperatures is that treatment efficiencies are reduced or detention times are increased. Using the following equation, the detention time necessary to meet a given removal efficiency at a known reaction rate constant can be determined.

$$t = \frac{E}{2.3\,k_1\,(100 - E)}$$

where:

t = detention time, days

E = removal efficiency, %

k_1 = Biological rate constant (base 10)

Table 8. Biological temperature coefficients, θ

Process	θ Range	Temp range °C
Stabilization pond	1.072 - 1.085	3 - 35
Activated sludge	1.0 - 1.041	4 - 45
Aerated lagoon	1.026 - 1.058	2 - 30
Trickling filter	1.035	10 - 35
Aerobic-facultative lagoon	1.06 - 1.18	4 - 30
Anaerobic lagoon	1.08 - 1.10	5 - 30
Extended aeration	1.037	10 - 30

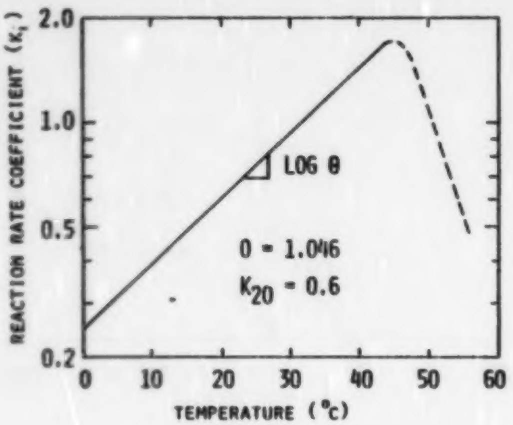


Figure 9. Effect of temperature on reaction rates.

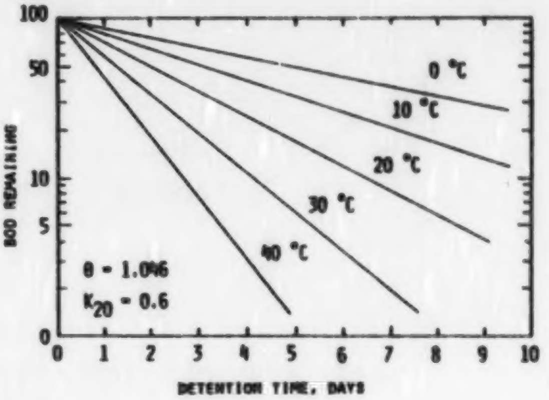


Figure 10. Effect of temperature on treatment efficiency.

The effect of temperature on the detention time and percent BOD removal are presented in figure 10. As the temperature drops in a treatment unit—such as a stabilization pond, the required detention time to reach the desired BOD removal is greatly increased. The net effect is a large increase in size and cost of unit.

In addition to the effects on biological activity due to variations in the reaction rate constant, k_1, temperature also effects the oxygen transfer rate and the solubility of oxygen in the water. Wind velocities will affect the rate of surface reaction, and solar radiation will affect the photosynthesis reactions. Ultimately, all of these factors affect the rate of biological activity.

CONCLUSIONS

Climatic effects are one of the items that should be considered in the development of any control technology program. While not all aspects of the climate will adversely affect the treatment efficiency of a given unit operation, the physical and electrical design aspects may require special attention to prevent malfunctions of their operations.

The climate of an area will affect the selection of the treatment sequence to reach desired effluent limitations. Too many environmental assessments are being prepared that assume that a biological process will dispose of all the wastes when this may not be true. Awareness of the potential problems and a more thorough evaluation of the design problems may take care of the climatic effects on wastewater treatment.

REFERENCES

1. J. M. Ramirez, "Meteorology/Air Quality Aspects of a Coal Gasification Plant in Dunn County," Project No. 2520-513-4886, Department of Soils, North Dakota State University, to be completed June 1976.
2. J. M. Ramirez, "Implications of the Atmospheric Environment on Coal Development in Western North Dakota," Project No. 16-418-GR, Subcontract No. ND 2535-4692, Department of Soils, North Dakota State University, to be completed May 1978.
3. W. Wesley Eckenfelder, Jr., and A. J. Englande, "Temperature Effects on Biological Waste Treatment Processes," International Symposium on Water Pollution Control in Cold Climates, p. 180, Water Pollution Control Research Series, 16100 EXH 11/71, U.S. Environmental Protection Agency.

WASTE MANAGEMENT OF FUELS PROCESSING EFFLUENTS

G. W. Grove*

Abstract

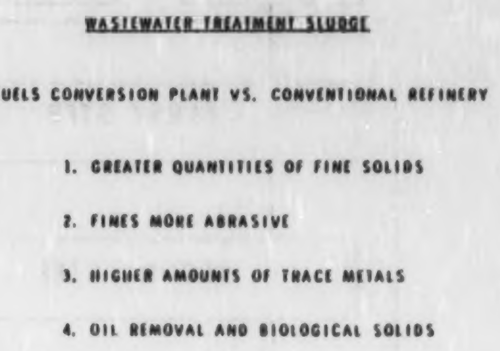
Refining of hydrocarbon fuels results in wastewater streams containing hydrocarbons, solids, and water. These contaminents must be removed from the water prior to discharge or reuse. Whether resulting from synthetic or conventional fuels refineries, the techniques for concentration and disposal of waste hydrocarbons and solids should be much the same. These techniques involve a series of concentration steps resulting in a reduced volume of sludge that can be treated in the lowest cost environmentally acceptable manner.

This paper describes technology developed in the last several years for refinery wastewater treatment sludge concentration. The advantages compared to previously used techniques are:

1. *Less energy consumption.*
2. *Lower investment and operation cost.*
3. *Higher sludge concentration which reduces final sludge treatment or disposal cost.*
4. *Improved separation of waste and water.*

Over the last several years Exxon Research and Engineering has improved the technology for concentrating oily solid contaminants which result from treatment of refinery wastewaters. The dewatering of these sludges is essential to reduce the volume and therefore disposal cost of the waste material. This paper compares wastewater sludges resulting from conventional refinery and synthetic fuels wastewater treatment plants. It will then describe application of new sludge concentration technology for dewatering of these effluent sludges.

The exact composition of effluents from synthetic fuels conversion plants has not been well defined and in fact will vary widely depending on the source of synthetic fuel and the conversion process used. However, several general comparisons can be made with effluents from conventional refinery wastewater treatment plants (fig. 1).



WASTEWATER TREATMENT SLUDGE

FUELS CONVERSION PLANT VS. CONVENTIONAL REFINERY

1. GREATER QUANTITIES OF FINE SOLIDS
2. FINES MORE ABRASIVE
3. HIGHER AMOUNTS OF TRACE METALS
4. OIL REMOVAL AND BIOLOGICAL SOLIDS

Figure 1. Wastewater treatment sludge.

1. Larger quantities of fine solids may be anticipated due to coal cleaning, grinding, and drying operations. Portions of these solids will be present in the wastewater.
2. Fines from stone, refuse, and slag are likely to be more abrasive than solids found in conventional refinery water effluents.
3. Higher levels of trace metals in coal and shale will require greater concern about leaching from waste sludges at landfill sites. This is especially true since acidic nature of the waste may increase solubility of these metals. Leaching problems can be minimized by reducing the volume of sludge disposed on the land.
4. The BOD and insoluble oil content of synthetic fuel plant wastes will depend largely on the conversion process and temperatures involved. However, for liquefaction processes, it can be assumed that process water will contact liquid hydrocarbons and oil removal and biological treatment of the wastewater will be required.

Based on these assumptions, wastewater from fuels conversion plants will be similar to refinery wastewater in that it will contain fine inert solids, biological solids, and insoluble oil. There will likely be greater quantities of abrasive solids with higher trace metal concentrations.

A typical process sequence for removal of wastewater contaminants is shown across the top of figure 2. The processes used for removal of these contaminants include dissolved air flotation, granular media filtration, biological treatment, and activated carbon. All of these processes result in dilute slurries of 0.1-5.0 weight percent oily solids. These slurries must be concentrated to reduce the large volumes of water retained with the fine solids.

The oily solids from these treatment processes are concentrated in a series of steps shown within the dotted line. In a typical refinery, the area within the dotted line

---

*The author is with Exxon Research and Engineering Co., Florham Park, New Jersey 07932.

Preceding page blank

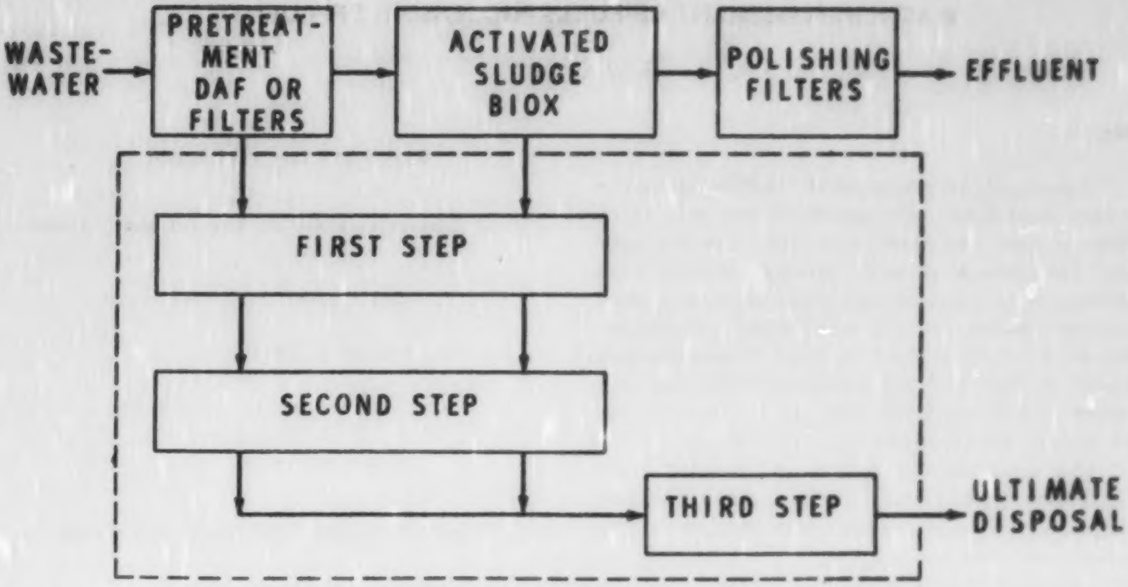


Figure 2. Typical refinery or chemical plant wastewater treatment.

accounts for 40 percent of the investment and 60 percent of the operating cost of the wastewater treatment plant.

Figure 3 shows the concentration steps in more detail. First the sludge is concentrated by gravity settling or flotation. These are relatively low cost processes per unit volume of sludge treated. Next, the sludge is further concentrated mechanically. Traditionally centrifuges, pressure, and vacuum filters have been used for mechanical dewatering. These higher cost processes, along with the newer technology of gravity belt filtration, will be discussed later in more detail. Finally, incineration may be used to reduce sludge volume to an absolute minimum or the sludge may be disposed directly to the land. In either case, it is important to reduce the volume of sludge being disposed in order to minimize cost and environmental problems.

Recent studies at Exxon Research and Engineering have concentrated on mechanical dewatering because of the critical technology needs of equipment used for this purpose. We have found that gravity belt filtration has significant advantages compared to previously used centrifuges, pressure, and vacuum filters. It will also be shown how gravity belt filtration enables greater flexibility in design of the entire wastewater treatment system. This increased flexibility can result in considerable investment and operating cost savings.

First Step	Second Step	Third Step
Gravity Settling	Filtration Vacuum	Landfill
Flotation	Pressure	Sludge Farming
	Centrifugation Scroll	Sand Lime
	Disc Imperforate Basket	Incineration
	Gravity Belt Filtration	

Figure 3. Methods on concentration.

Figure 4 describes some of the problems associated with conventional mechanical dewatering equipment. Vacuum or pressure filters have not been used extensively for refinery sludges because filter surfaces blind rapidly. This necessitates adding additional inert solids to increase porosity and results in increased solids for disposal by factor of two to three. Centrifuges have been used more extensively for concentrating petroleum and

- VACUUM AND PRESSURE FILTERS
  - HIGH ΔP BLINDS CLOTH
  - ADDITION OF INERT SOLIDS INCREASES DISPOSAL COST

- CENTRIFUGES
  - HIGH SPEED MACHINES RESULT IN ABRASION AND PLUGGING
  - LOW SERVICE FACTOR AND HIGH MAINTENANCE COST

Figure 4. Problems of mechanical dewatering.

petrochemical sludges. These are high-speed, precision machines. The grit in the sludge can cause rapid erosion and in some cases plugging. This results in frequent downtime for maintenance and cleaning.

Now I would like to discuss gravity belt filtration for concentration of refinery and petrochemical wastewater sludges. These devices have been used in Europe for 10 to 12 years on municipal sludges, but application to oily refinery sludges is yet to be proven commercially. Our studies were carried out on one gravity belt filter press that is manufactured both in Europe and the United States. It is similar to presses manufactured by several U.S. companies.

Gravity belt filter presses dewater sludge in three basic steps. First, polymers are added to flocculate the fine sludge particles. Next, the flocced feed is poured onto a coarse screen where the clear water readily drains away. Third, the cake is pressed slowly to remove additional water. Figure 5 shows a schematic of the press. Polymer is added to the sludge in a rotating drum where the floe is formed. Water then drains from the sludge on the top belt. At the end of the top belt, sludge falls to the bottom belt and is pressed between the two screens. The rate at which pressure is applied is very important. If pressure is applied rapidly, the sludge goes through the screen. However, if pressure is applied gradually, additional water drains from the sludge and solids concentration in the cake increases.

We have tested a full scale gravity belt filter press at Exxon's Bayway and Benicia Refineries. In our tests, we were interested in four parameters: (1) solids production rate, (2) solids capture, (3) properties of the cake, and (4) polymer dosage and costs.

Based on the full scale tests, it was determined that production rate is a functinn of feed concentration. Feed concentration was determined by drying a small representative sample of the feed at 103° C to determine dry solids concentration. This "dry solids" therefore includes true solids as well as higher boiling hydrocarbons (fig. 6).

At low feed concentrations there is a constant filtrate flow rate determined by resistance of the screen to filtrate flow. Production rate is therefore proportional to feed concentration. At higher feed concentrations, filtrate flow rate decreases due to increased resistance of the thicker sludge blanket to filtrate flow. Production rate continues to increase, but at a slower rate. Specific production rates may vary depending on the specific sludge and gravity belt press manufacturer. The machines will operate at any rate up to these values and rate does not depend on the ratio of oil to solids in typical feed.

Solids capture has been found to be very high for gravity belt filter presses compared to centrifuges. Filtrate plus wash water, from biological sludges has contained as low as 100 ppm solids. This is a solids capture of about 99.7 percent. Solids capture for oily sludges is about 97-98 percent. These numbers compare to solids capture of 86-92 percent encountered using imperforate basket centrifuges.

Gravity belt filter presses use the normal water treating high molecular weight anionic and cationic polymers. The flocculation of sludge does not appear to be very sensitive to the amount of polymer used. There is an optimum dosage from a cost standpoint, but operation is not adversely affected by minor changes in sludge composition and minimum operator attention is required.

Polymer costs derived from our studies are in the range of $2 to $10 per ton of dry solids. High polymer cost results from dilute feeds and can generally be reduced by gravity settling or dissolved air flotation ahead of the press. Combining sludges has also resulted in reducing polymer cost 10 to 25 percent compared to handling the sludges separately. This is probably due to neutralization of electrostatic charges in the feed. Therefore, combining sludges may not always result in lower cost but it should never result in increased cost.

Cake concentrations obtained with gravity belt filter presses have been two to three times that obtained with imperforate basket centrifuges. This is the primary advantage of gravity belt filtration since it greatly reduces incineration or final disposal cost.

Figure 7 gives a comparison of gravity belt filtration and our previously preferred mechanical dewatering device, the imperforate basket centrifuge.

- The use of gravity belt filtration indicates lower investment compared to centrifuges for refineries

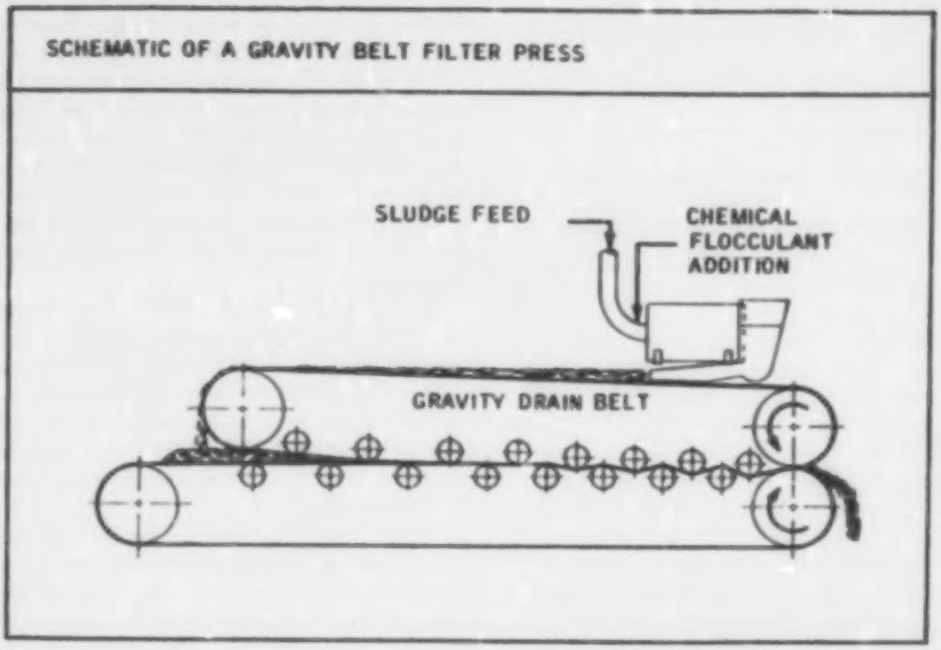

SCHEMATIC OF A GRAVITY BELT FILTER PRESS
SLUDGE FEED
CHEMICAL FLOCCULANT ADDITION
GRAVITY DRAIN BELT

Figure 5. Schematic of a gravity belt filter press.

we have studied. This is due to the lower installation cost of these slow speed, low horsepower devices. Operating costs are about even since the higher polymer cost is offset by reduced power cost.

European experience with municipal sludge shows lower maintenance and high service factor. About 95 percent service factor is estimated for gravity presses as opposed to 85 percent for centrifuges. Also, much of the maintenance can be done by the operators whereas skilled machinists are required for centrifuge maintenance.

As mentioned, a major advantage of gravity belt filtration compared to imperforate basket centrifuges is that the cake produced is more concentrated. Note that a centrifuge will not concentrate DAF float as well as filter backwash whereas the gravity press concentrates both sludges equally well. This enables use of DAF pretreatment rather than granular media filtration and may result in a considerable investment savings.

- The dryer cake also reduces the amount of water to be evaporated in an incinerator resulting in a considerable fuel savings. Many locations haul sludge to offsite disposal. In that case, hauling cost savings would be directly proportional to the volume reduction in the amount of sludge.

The above applications are for concentration of wastewater treatment sludges. These sludges may be oily, slimy and gelatinous, which will plug vacuum and pressure filter media. Also, the specific gravity of the solids removed is close to that of water so that centrifugation is difficult. Part of our program has evaluated use of gravity belt filtration to remove water from FLEXICOKER venturi scrubber fines. FLEXICOKING is a fluid coking process followed by gasification of the cake. The hard abrasive nature of these coke fines from the scrubber are likely to be duplicated in synthetic fuels conversion plants and would result in severe abrasion of high speed centrifugal equipment.

Tests on a full scale gravity belt filter press showed

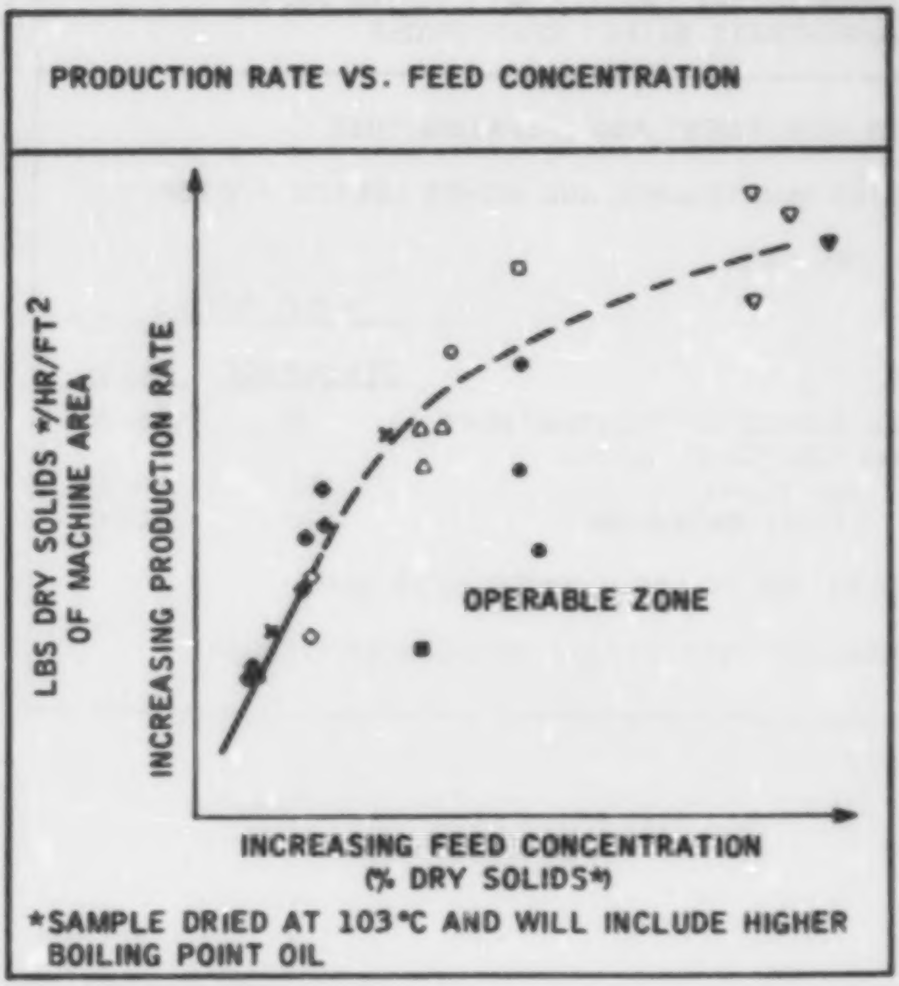


Figure 6. Production rate vs. feed concentration.

COMPARISON OF THE GRAVITY BELT FILTER PRESS WITH IMPERFORATE BASKET CENTRIFUGES

- LOWER INVESTMENT AND OPERATING COST
- REDUCED MAINTENANCE AND HIGHER SERVICE FACTOR
- VERY DRY CAKE

	% DRY SOLIDS	
	CENTRIFUGE	GRAVITY PRESS
BIO SLUDGE NO PRETREATMENT	9	18-20
PRETREATMENT SLUDGE		
DAF FLOAT	11	30-35
FILTER BACKWASH	20	30-35

- ENABLES USE OF LOWER INVESTMENT DAF
- INCINERATOR FUEL SAVINGS OR REDUCED DISPOSAL COST

Figure 7. Comparison of the gravity belt filter press with imperforate basket centrifuges.

that production rates were six times higher than rates obtained on wastewater treatment sludges. Production rate was a function of feed concentration, but cake solids concentration was independent of feed concentration. The cake was 44 percent solids vs 37 percent obtained by vacuum filter tests. Solids recovered were 98 percent.

In summary, our studies of mechanical dewatering have shown that there are significant incentives for using gravity belt filtration on refinery and chemical plant sludges. Synthetic fuel plants are likely to have wastewater sludges similar in some respects, but with more abrasive fine solids. Removal of these solids can easily be done by gravity belt filtration.

CONTROL TECHNOLOGY R&D NEEDS*

C.E. Jahnig, R. R. Bertrand, E. M. Magee†

Abstract

This paper discusses research and development needs in environmental control technology related to fossil fuel conversion operations. In some cases, existing control systems are inadequate or leave significant room for improvement in pollution control or in energy conservation. In other cases, existing information may be inadequate and additional work is needed to define and evaluate environmental aspects. Such items are discussed for the major areas of coal preparation, acid gas removal, sulfur recovery, methanation, wastewater treatment, and trace elements. These areas of concern are common, or are at least similar, in the various conversion processes being developed.

Technology needs developed as a result of extensive studies include the following:

1. *Indirectly heated coal dryer (e.g., fluid bed) which contains dust and also recovers water from moisture in coal.*
2. *Objectives are defined for improved acid gas removal systems, including hot gas cleanup.*
3. *Methanation systems to optimize recovering the heat of reaction, equal to 20 percent of the HHV of reactants.*
4. *Techniques to minimize water consumption, and for wastewater cleanup and reuse.*
5. *Handling of trace elements, especially the large amount of volatile ones that leave the gasifier and are carried into the gas cleanup system.*

INTRODUCTION

There are many different conversion processes for making clean liquid or gas fuels from coal, but many of the environmental concerns and problems are quite similar. This is not surprising since every process starts with coal as the raw material and rejects sulfur and ash, while generating a wastewater stream that contains a broad spectrum of contaminants. In order to facilitate environmental assessments, we have developed a generalized basis which broadly represents the operation of gasifying with steam and oxygen (ref. 1). The model provides typical heat and material balances and flow rates to use as an overall framework in environmental evaluations.

Although the various coal conversion processes are distinctly different, they also employ a number of common operations, such as coal preparation, acid gas removal, waste water treatment, and provision for utilities such as electric power, steam, and water (table 1). For all of these common areas, careful planning is required in order to assure that the operations are environmentally satisfactory. We believe that the areas of environmental concern can be properly taken care of, but they need to be examined and evaluated early in the development program so that the required work can be done in an orderly manner and not under the pressure of a crisis. A program and procedures for this have been developed (ref. 2).

Table 1. Areas for improvement

Coal preparation
Acid gas removal
Methanation
Wastewater cleanup
Trace elements
Energy and water conservation

In some areas of environmental concern, present technology is not completely adequate, as in the cases of acid gas removal and wastewater cleanup. In other areas environmental control technology is available, but there is considerable room for improvement—for example in coal drying, methanation, and overall aspects of energy conservation.

The area of trace elements deserves special mention because available information is not sufficient at this time to allow making a sound evaluation of potential environmental problems. Some of the trace elements in coal are appreciably volatile at gasification conditions and will be carried into the gas cleanup system where they may have to be removed and disposed of. Although

---

*This work was carried out under Contract No. 68-02-0629, U.S. Environmental Protection Agency.

†The authors are with the Government Research Laboratories of Exxon Research and Engineering Company, Linden, New Jersey.

trace elements are a major concern, the associated requirements for control technology can hardly be defined until more information is obtained on their amounts, where they appear, and in what form.

Research and development needs for control technology will now be defined in more detail for some specific areas that are common to most of the coal conversion processes. Starting with coal drying, it is a large operation which consumes fuel equal to 5 to 10 percent of the total coal (table 2). A desirable objective is to save this fuel by using low level waste heat for drying the coal. There is more than enough waste heat available from the process and the need is to devise practical methods for its use. One possibility is to contact the coal with warm flue gas from the utility boiler or a process furnace. This may be particularly applicable if stack gas cleanup is used subsequently, thereby controlling dust emissions. Another possible source of heat is warm air from an air-fan cooling unit, some of which are large enough to supply all of the required heat.

Table 2. Coal preparation

Fuel used may be 5-10% of total coal.

Consider fluid bed dryer using waste heat.

On lignite, water from drying can amount to half of plant makeup.

Refuse from coal cleaning may be 400-800 acre ft/yr.

One type of drying system to consider is indirect heating using coils in a fluidized bed of coal (ref. 3). This greatly reduces the volume of gas that must be cleaned up, although it will also be somewhat more difficult to accomplish drying in the presence of an offgas having higher moisture content. A potential advantage is that water can be recovered from the drying operation by using a simple air cooler on the vent gas. In plants using lignite coal containing 30 percent or more moisture, water recovered from the dryer can contribute 50 percent of the total water makeup required for the plant.

Work is needed on disposing of solid wastes from coal conversion, including waste from coal cleaning as well as ash or char. This may not be as complex a technical problem as the gasification or liquefaction process, but the volume of material to dispose of is enormous and can cause concern regarding dust, leaching, revegetation, and land use. Refuse from coal cleaning can amount to 25 percent of the run of mine coal, equal to 400-800 acre feet/year for a large plant. In addition residual ash may be 10-20 wt. percent of the coal converted. If gasification takes place without a change in particle size, the volume of ash can be as much as the volume of coal used. A slagging operation should decrease the ash volume and also would minimize the disposal problems due to dusting or leaching. Here is an area that has opportunities for land improvement.

Moving on to the subject of acid gas removal, it appears that available technology can probably provide acceptable environmental controls, but with considerable difficulty; and there is room for improvement with regard to energy consumption. Research objectives can be spelled out as follows for an ideal process:

1. Remove all forms of sulfur to a low level.
2. Provide a concentrated H_2S stream (50 vol. percent) to sulfur plant.
3. Assure that the CO_2 reject stream is clean and free of sulfur, combustibles, etc.
4. Have low consumption of utilities and energy.
5. Generate no chemical wastes to be disposed of.

In some applications, it is also very desirable to make a sharp separation between H_2S and CO_2, beyond the capability of current technology.

Acid gas removal systems based on amines are not effective on carbonyl sulfide, which may account for perhaps 10 percent of the total sulfur in the raw gas from gasification. Contaminants such as HCN interfere with regeneration of amine. Hot carbonate can partially remove carbonyl sulfide, but it is very difficult to provide a concentrated H_2S stream and at the same time have a clean CO_2 stream that can be vented directly to the atmosphere. It may be that all the various sulfur compounds could be hydrolyzed efficiently to H_2S over a bauxite catalyst at 500-700°F ahead of acid gas removal to facilitate sulfur removal, or a hydrolysis catalyst might be incorporated in the scrubbing system. Scrubbing with refrigerated methanol is used in some proposed plants, but the separated H_2S is shown to be mixed in the rejected CO_2 at very low concentration, along with 1-2 vol. percent of combustibles (refs. 4,5). Cleanup of this stream will be complicated.

A Claus plant is usually included to recover byproduct sulfur. An alternative is absorption/oxidation which combines absorption of H_2S with oxidation to make byproduct sulfur via a liquid phase Claus type reaction (ref. 6). This alternative has the advantage that it can give high conversion to sulfur even at a very low H_2S concentration. Unfortunately, it is not effective on carbonyl sulfide or other sulfur compounds, and lacks the incineration of combustibles inherent in a Claus plant.

On a Claus plant, the volume of tail gas increases as the concentration of sulfur compounds in the feed gas is decreased (table 3). Therefore a larger volume of tail gas must then be cleaned up to a lower sulfur level in order to maintain the same tons/day of sulfur emission. For example, with a feed of 25 vol. percent H_2S the tail gas volume is two times what it would be at 100 percent H_2S. At 15 percent H_2S the volume is threefold, and at 10 percent H_2S it is fourfold. The latter levels are encountered in some gasification designs.

In a typical plant making SNG, the weight of CO_2 rejected to the air from acid gas removal is roughly equal to the total amount of coal gasified. Consequently, it is very important that the CO_2 stream be clean and free of contaminants or odors. It is quite difficult to assure a low sulfur level, and some study designs have shown up to 3,000 ppm H_2S, which is excessive. Other designs based on scrubbing with refrigerated methanol show 1-2 vol. percent of combustibles in the CO_2 vent stream, including ethane and CO. Incineration is one way to destroy combustibles, but the amount is not sufficient to support combustion in a furnace, although it may amount to 3,000 MM Btu/day or over 1 percent of the SNG heating value. Using extraneous fuel for incineration could introduce a large debit, but it might be avoided if catalytic combustion can be applied—possibly with heat exchange for preheat and recovery. Recovery of this heating value is a technological challenge, and an environmental objective.

Table 3. Want to remove sulfur first, then CO_2

Vol. % H_2S to Claus	Vol. Tail Gas (Ratio)
100	1
50	2
15	3
10	4

CO_2 rejected to air = wt. of coal gasified

1% combustible content = 1% of coal HHV

An important objective is lower utilities and energy consumption for acid gas removal. It usually represents one of the largest consumers of utilities in the plant, comparable to the oxygen plant. In optimizing the utility balance, heat pumps should be evaluated so that the heat of condensation on the overhead can be used to supply heat to the reboiler. The theoretical thermodynamic work for the separation is quite small, so it is possible that better techniques can be developed. Semipermeable membranes that are selective to CO_2 or to sulfur compounds represent one approach.

Removing sulfur at higher temperature may also have advantages. Techniques are known for removing small amounts of sulfur using metals or metal oxides such as iron, zinc, copper, or nickel. The difficulty has been that these cannot be conveniently regenerated as required for removing large amounts of sulfur. It should be possible to develop practical techniques for regeneration so that the sulfur absorbent could be recycled continuously or used batchwise. Limestone and dolomite have been tested for this purpose, and the results are very encouraging (refs. 3,7). Incidentally, in applications such as the combined cycle for power generation, it is neither necessary nor desirable to remove CO_2 along with sulfur.

One final comment on acid gas removal—most systems need an appreciable amount of makeup chemicals, which can then show up as plant effluents. Often there is a purge or chemical waste stream to reject products of side reactions or stable compounds formed with contaminants that cannot be regenerated adequately. Chemical waste streams can be a disposal problem and should be minimized or eliminated.

The next area for discussion is methanation (table 4). Reaction of CO and H_2 to make methane has a very high heat release, equal to 20 percent of the heating value of the reactants. This serves to emphasize that low Btu fuel gas should be used where possible rather than SNG. The loss of 20 percent in heating value is not an entirely real loss when making SNG, since it is used to make high pressure steam which would otherwise have to be made in a boiler. Conventional methanation uses a fixed bed of catalyst, making it difficult to remove the large amount of heat and to provide good temperature control. Gas is recycled from the reactor outlet through waste heat boilers and back to the reactor inlet, with a considerable power consumption on the recycle gas compressors. Recent test work has shown that methanation can be carried out in a fluidized bed or in a slurry reactor (ref. 8). These look promising in that the reaction heat should be recoverable at a higher temperature level using exchanger surface in the reactor, while eliminating

Table 4. Methanation

Heat release is 20% of HHV in reactant.

Recover steam, but recycle compressor is large.

Slurry or fluid bed reactor avoids compressor.

Methanation and shift might be combined.

---

the need for recycle gas compressors to control reactor temperature. In the slurry operation, water gas shift has been found to occur during methanation; thus the two reactions might be carried out in one reactor so that the water produced by methanation is available to provide that consumed by the water gas shift reaction.

The ultimate extension of this would be to carry out all methanation in a shift reactor ahead of acid gas removal. In effect, CO would then be reacted with steam to form methane and CO_2. Hot sulfur removal would probably be needed first. If practical, this arrangement would mean that the gas only has to be cooled once and not reheated, whereas with conventional methanation, the gas is cooled for sulfur removal, reheated for methanation, and cooled again. A limitation in the proposed simplification is that methanation would have to be selective in the presence of CO_2, but the subsequent CO_2 removal should be easier in view of the decreased gas volume to be scrubbed.

One of the major environmental problems on coal conversion is the cleanup and disposal or reuse of wastewater (table 5). The sour water condensed from the raw gas may contain a wide variety of sulfur, nitrogen, and oxygenated compounds, together with dust and oil or tar (ref. 9). In addition it is expected that various trace elements will be present in the sour water, and may have to be separated or deactivated. Extensive processing will be needed to make the wastewater suitable for discharge to the environment, in which case it will represent a very desirable makeup water for the plant.

A probable sequence of processing steps to clean up sour water is as follows:

1. Sour water stripper to remove H_2S, NH_3, CO_2, light gases.
2. Settler to remove solids and skim off oil.
3. Extraction of phenols (if required).
4. Biological oxidation (biox) to consume residuals.
5. Sand filter, activated carbon, etc.

The major R&D need on wastewater cleanup is to demonstrate that the selected systems will give adequate cleanup under realistic conditions. This will no doubt require operating with actual streams from an operating plant or pilot plant, since the array of possible contaminants is so complex that it may be impractical to prepare a synthetic mixture, or to predict performance of treating operations.

Table 5. Wastewater – contaminants

Sulfur compounds:
H_2S, sulfate, thiosulfate

Nitrogen compounds:
ammonia, cyanides

Oxygenated compounds:
phenols, acids

Other:
hydrocarbons, carbonates, chlorides

A possibility to consider (figure 1) is not to clean up the sour water, but rather convert it to steam which would be fed to the gasifier. Although conventional steam generators may not be applicable due to fouling and corrosion, it should be possible to vaporize the sour water by injecting it into a bed of hot fluidized solids which are heated indirectly (ref. 10).

Regarding trace elements, a large number may be present in the various coal feeds, and many of them are toxic. Many of the trace elements are volatile to some extent at gasification conditions and can then be carried into the gas cleanup system where they may cause complications (table 6). Considerable information is available on the amount of minor and trace elements in various coals (ref. 11), and a limited amount of work has been done to determine the percent volatile for specific elements at gasification conditions (ref. 12). To make the picture more meaningful, the amount of certain trace elements in a typical coal have been combined with the estimated percent volatile to give the amount in pounds per day that may be carried out of the gasifier with the raw gas. Results are shown on table 6 for a coal feed rate of 12,000 tons/day. Volatility of chloride has not been specifically measured for gasification but it is known that during combustion it is nearly all volatile. The combined amount of trace elements that may be volatile and

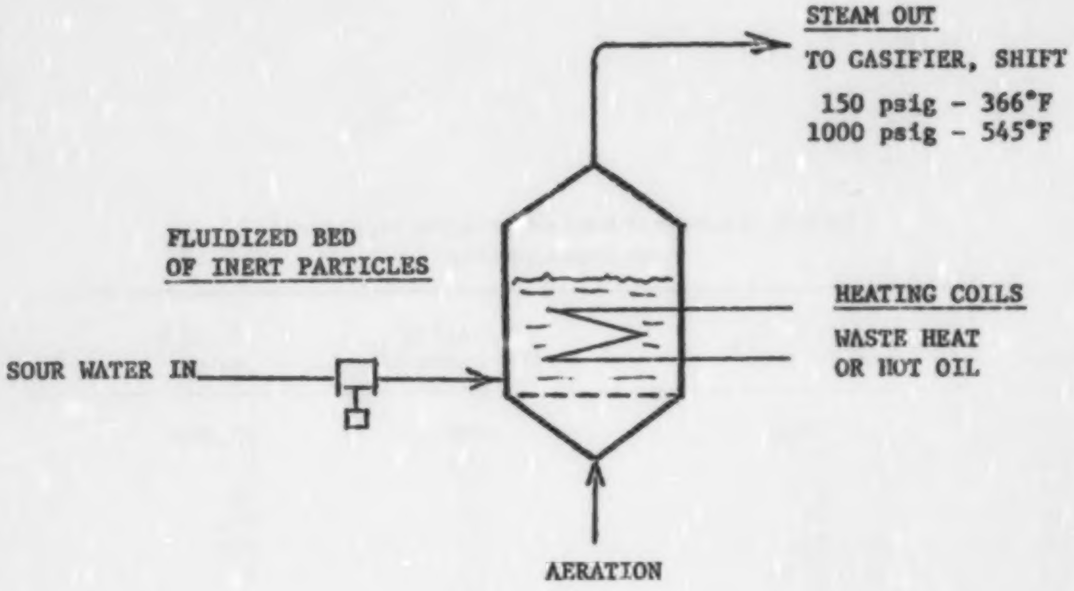

STEAM OUT
TO GASIFIER, SHIFT
150 psig - 366°F
1000 psig - 545°F
FLUIDIZED BED
OF INERT PARTICLES
HEATING COILS
WASTE HEAT
OR HOT OIL
SOUR WATER IN
AERATION

Figure 1. Make steam from sour water.

may have to be handled in the gas cleanup system is quite formidable. Obviously this can pose serious problems if not adequately considered early enough in the development of a coal conversion process. Much more information is needed to define the situation and show where trace elements appear and in what form. Systems can then be worked out for deactivating or separating them where necessary.

As a final point on R&D needs, mention should be made of the need to conserve energy and water. A few items in this category are shown in table 7. Without going into details, these serve to show some approaches that may lead to savings in energy and water consumption, as well as stimulate thinking in this important area. Other suggestions are given in a series of 14 reports covering our environmental assessments made for the Environmental Protection Agency (refs. 2,3,10, etc.).

Table 6. Example of trace elements that may appear in gas cleaning section

Element	Possible ppm in coal[a]	% Volatile for example[b]	In gas lb/day[c]
Cl	1500	>90+	32,400
Hg	0.2	90+	5
Se	2.2	74	39
As	31	65	484
Pb	7.7	63	116
Cd	0.14	62	2
Sb	0.15	33	1
V	35	30	252
Ni	14	24	81
Be	2	18	9
Zn	44	(10)	106
B	165	(10)	396
F	85	(10)	204
Ti	340	(10)	816
Cr	22	nil	nil

[a] Mainly based on Pittsburgh Seam Coal.

[b] Mainly based on lower temp gasifier (ref. 12) and indicated at 10% for Zn, B, and F, in absence of data.

[c] For 12,000 tons/day of coal feed.

Table 7. Energy conservation

Heat pump--AGR and S.W. stripper
Furnace air preheat and low excess air
Process preheat by heat recovery
Recovery from high pressure gas/liquid
Burn high S coal using stack gas cleanup
Water conservation
Air cooling
Heat pump
Recover moisture in coal
Separate water from sales in wastewater

REFERENCES

1. R. R. Bertrand and C. E. Jahnig, "Environmental Aspects of Coal Gasification," presented at AIChE Meeting, Sept. 8, 1975, Boston, Mass. (to be published).
2. C. D. Kalfadelis, E. M. Magee, G. E. Milliman and T. D. Searl, "Evaluation of Pollution Control in Fossil Fuel Processes, Analytical Test Plan," EPA-650/2-74-009, October 1975.
3. C. E. Jahnig and E. M. Magee, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification: CO_2 Acceptor Process," EPA-650/2-74-009d, Dec. 1974 (NTIS PB-241 141).
4. El Paso Coal Gasification Project - Environmental Impact Statement, 1974.
5. T. E. Berty and J. M. Moe, "Environmental Aspects of the Wesco Coal Gasification Plant," Proceedings of EPA Symposium, St. Louis, Mo., EPA-650/2-74-118, Oct. 1974.
6. J. E. Ludgerg, "Removal of Hydrogen Sulphide from Coke Oven Gas by the Stretford Process," 64th Annual Meeting of the Air Pollution Control Association, June-July 1971.
7. R. C. Hoke and R. R. Bertrand, "Pressure Fluidized Bed Combustion of Coal," Institute of Fuel Symposium, Paper No. 18, Sept. 1975, London.
8. M. B. Sherwin, "Progress in Liquid Phase Methanation," Seventh Synthetic Pipeline Gas Symposium, Oct. 27-29, 1975, Chicago, Ill.
9. A. J. Forney, W. P. Haynes, S. J. Gasior, G. E. Johnson, and J. P. Strakey, "Analyses of Tars, Chars, Gases and Water Found in Effluents from the Synthane Process," Bureau of Mines, TPR 76, January 1974.
10. C. E. Jahnig, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification: BI-GAS Process," EPA-650/2-74-009g May 1975 (NTIS PB-243 694).
11. R. R. Ruch, H. J. Gluskoter, and N. F. Shimp, "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," EPA-650/2-74-054, July 1974.
12. A. Attari, "The Fate of Trace Constituents of Coal During Gasification," EPA-650/2-73-004, August 1973.

Session IV:

PROCESS MEASUREMENTS

James A. Dorsey
Session Chairman

MEASUREMENT PROGRAMS FOR ENVIRONMENTAL ASSESSMENT

R. M. Statnick, Ph.D. and L. D. Johnson, Ph.D.*

Abstract

The current energy shortage and the public's demand for environmentally safe energy conversion processes have focused the attention of both the public and the private sectors on the potential environmental problems which are associated with these technologies. An environmental assessment test strategy has been developed by the Process Measurements Branch, Industrial Environmental Research Laboratory, Research Triangle Park (IERL/RTP).

The proposed environmental assessment sampling and analytical test strategy consists of two distinctly different levels of effort. Level 1 is a survey phase which identifies the pollution potential of all process feed, product, and waste streams through chemical and biological testing. The second level of effort, Level 2, is characterized by quantative determination of potentially hazardous substances in process streams and by expanded bioassay of the process streams which were sampled. This paper describes the features of this environmental assessment sampling and analysis strategy and its associated costs.

INTRODUCTION

The sampling and analytical effort which supports an environmental assessment has its roots in the historical failure of both the public sector and the private sector to evaluate the environmental and the health effects of a given product or of a given technology. The most publicized example of this is the case of DDT. The chemical fulfilled a need—control of pests which were injurious to both humans and domesticated animals. As the full market potential of this chemical was realized, several scientists began to notice side effects arising from the use of DDT. Increased levels of DDT were found in humans, in drinking water, and in domesticated animals and wildlife. The weight of evidence was such that EPA banned the scale of DDT in the United States.

The energy shortage which grips the United States has focused attention on the development and full scale implementation of coal conversion technologies, on expanded use of substitute fuels for natural gas and oil, and on a variety of new energy related technologies. Each of these processes has associated with it a possible environmental insult. EPA has initiated a program to determine the magnitude of the potential environmental problems associated with the emerging energy technologies. The technology assessment program is called an integrated assessment and includes social, economic and environmental effects. The environmental assessment is a key input to an integrated assessment and provides environmental effects information on all process feed stocks, product streams, and waste streams. The type of information which is developed is based on extensive chemical analysis and bioanalysis of the appropriate samples. The details of these analyses are discussed later in the paper. The information which is developed by an environmental assessment program can be used for the purposes identified in table 1.

Environmental Assessment Testing Strategies

The Process Measurements Branch* has extensively examined two field test options for the performance of an environmental assessment. The analytical goals of each option were identical: 1. identification of specific inorganic and organic compounds, 2. cytotoxicity testing, 3. mutagenicity testing, and 4. carcinogenicity testing. Each option would acquire samples of each process feed stock stream, product stream, and waste stream in sufficient quantity to complete the rigorous chemical and biological test matrix. The basic difference between the two options is the mechanism used to achieve the goals, and the resultant cost effectiveness of each.

The first option considered is the direct approach. The operation involves the planning and the execution of a single comprehensive sampling and analysis effort.

Table 1. Selected uses of environmental assessment field sampling data

- Identify problematic process streams.
- Identify the physical characteristics (e.g. flow, temperature, physical state, etc.) of problematic streams.
- Assist in setting control technology R/D priorities.
- Provide data to health effects, monitoring, and integrated assessment programs.

---

*Industrial Processes Division, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina (Environmental Protection Agency).

Preceding page blank

The direct approach is philosophically attractive and has been examined on the basis of cost to implement at a constant level of information output.

The second option considered was a phased approach which requires two separate, distinct levels of sampling and analysis. Level 1 sampling and analysis has as its goal the gross identification of pollution potential of a source and to set sampling and analysis priorities for level 2. Level 2 sampling and analysis has as its goal the refined, accurate identification of specific pollutants in specific streams from a given source.

Assuming a constant level of information output, TRW Systems Inc. (ref. 1) has estimated the performance costs associated with the environmental assessment of a limestone wet scrubber and a coal gasifier. The cost comparisons are given in table 2. Based on this analysis, the phased sampling and analysis option was selected as the most cost effective mechanism for performance of an environmental assessment. The phased sampling and analysis option is detailed in the following text.

Phase 1
Environmental Assessment

The details of the phase 1 sampling and analysis effort are presented in other papers in this volume. This paper addresses the goals of phase 1 and the end uses of phase 1 data.

Since the objective of an environmental assessment is to identify any potential environmental pollution from a process, all process feed stocks, product streams, and waste streams will be sampled in level 1. For purposes of this paper, there are four categories of sampling (see table 3). The procedures which are used to acquire samples from each of these categories are described in the next paper (Lockmüller).

The samples which are acquired will be subjected to elemental analysis (inorganics), to liquid chromatography (organics), and to bioassay (cytotoxicity and mutagenicity). Elemental analysis are performed with a spark source mass spectrometer. The hydrocarbons are analyzed as follows: less than C_6 hydrocarbons by gas chromatography at the site and greater than C_6 hydrocarbons using liquid chromatography, gravimetry, and infrared analysis to provide organic class identification. The details of the analytical procedures are presented by Professor Lochmüller (this volume).

Table 2. Sampling and analysis cost summary

Process	Option	Sampling cost	Analysis cost	Total
		$	$	$
Limestone Wet Scrubber	Direct	58,400	365,894	424,300
	Phased	23,950	294,975	318,930
Coal Gasifier	Direct	205,560	2,872,000	3,077,560
	Phased	84,775	1,234,100	1,318,935

Table 3. Sampling categories

Particulate
All gas streams are assumed to contain particulate and $<C_6$ hydrocarbons.

Solids
tars, solids which include coal, ash, Bitumen, etc.

Liquids
include both organic, inorganic, and mixed liquors. This category includes slurries.

Fugitive Emissions
gaseous and liquid wastes which are not confined to ducts or to channels of regular area.

The results of the phase 1 effort are tabulated as mass emission rates, emission rate per unit of product, etc. The full assemblage of data, including chemical and biological, are used to prioritize the streams which have been sampled and to focus the level 2 sampling and analysis effort. The level environmental assessment can be used as input to direct control technology R/D efforts, to assist in health effects studies, and to aid in the planning of monitoring efforts.

Phase II
Environmental Assessment

The characteristics of a phase II environmental assessment are given in table 4. The streams which are sampled are those which received a priority rating as a result of level 1 efforts. Streams which are low on the priority scale may not be sampled. This concept is shown in figure 1.

Table 4. Characteristics of Phase II environmental assessment

- Analysis focuses on identification of specific compounds.
- Optimized sampling techniques are used for specific classes of pollutants or specific pollutants of interest.
- High overall sampling and analysis accuracy.
- Bioassay is expanded to include dose response and carcinogenicity testing (if the level 1 mutagenicity test is positive).
- Testing will be carried out under one representative process condition.

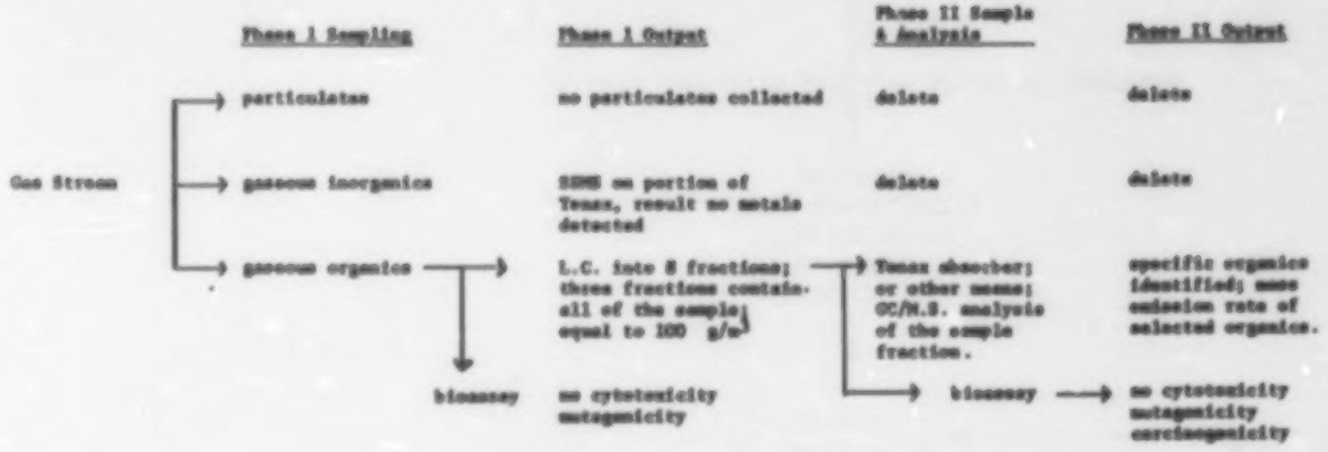

Phase I Sampling
Phase I Output
Phase II Sample & Analysis
Phase II Output
Gas Stream
particulates
no particulates collected
delete
delete
gaseous inorganics
SSMS on portion of Tenax, result no metals detected
delete
delete
gaseous organics
L.C. into 8 fractions; three fractions contain all of the sample; equal to 100 g/m³
Tenax absorber; or other means; GC/M.S. analysis of the sample fraction.
specific organics identified; mass emission rate of selected organics.
bioassay
no cytotoxicity mutagenicity
bioassay
no cytotoxicity mutagenicity carcinogenicity

Figure 1. Phased environmental assessment of gaseous sample containing no particulate material.

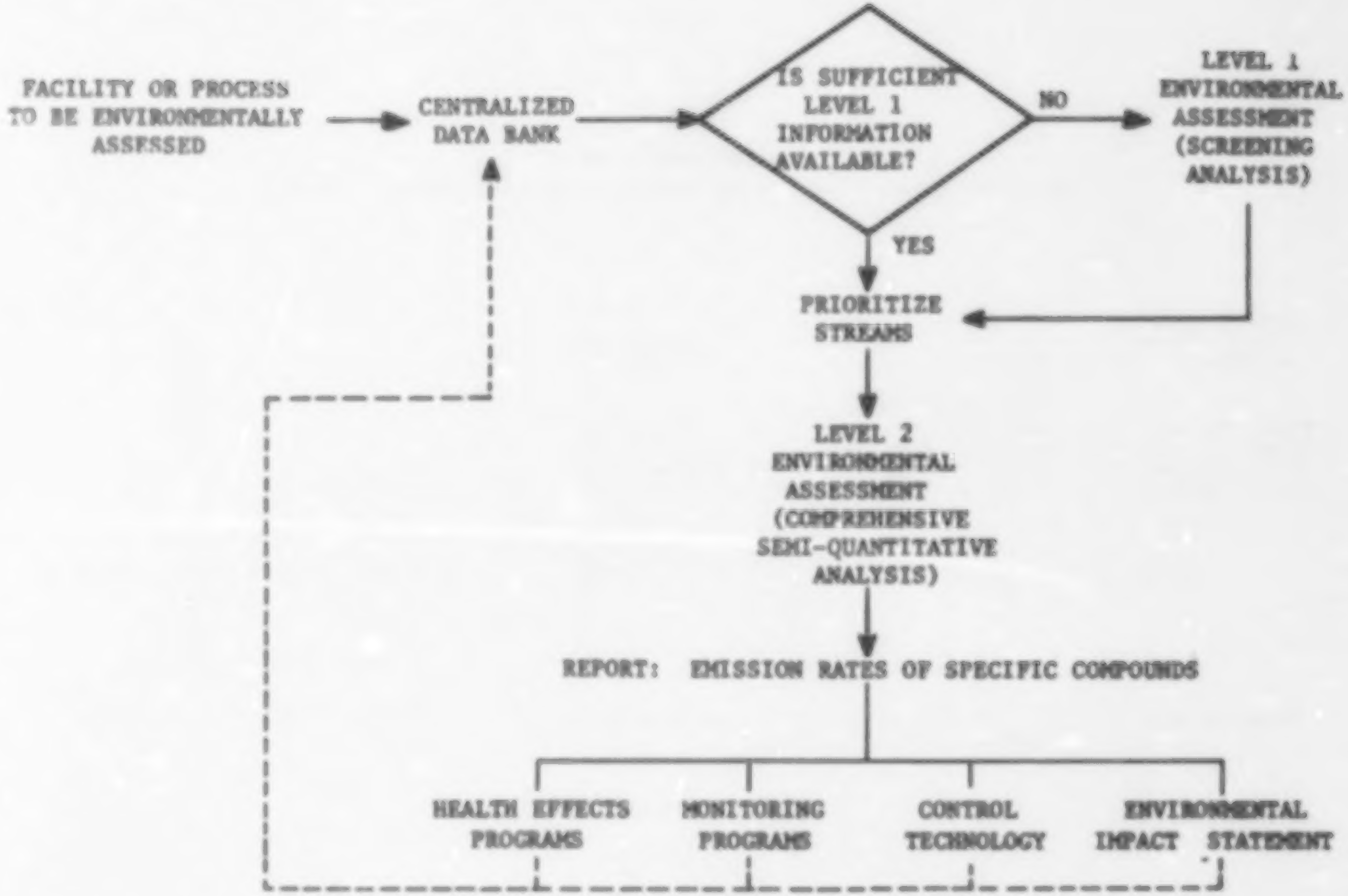

FACILITY OR PROCESS TO BE ENVIRONMENTALLY ASSESSED
CENTRALIZED DATA BANK
IS SUFFICIENT LEVEL 1 INFORMATION AVAILABLE?
NO
LEVEL 1 ENVIRONMENTAL ASSESSMENT (SCREENING ANALYSIS)
YES
PRIORITIZE STREAMS
LEVEL 2 ENVIRONMENTAL ASSESSMENT (COMPREHENSIVE SEMI-QUANTITATIVE ANALYSIS)
REPORT: EMISSION RATES OF SPECIFIC COMPOUNDS
HEALTH EFFECTS PROGRAMS
MONITORING PROGRAMS
CONTROL TECHNOLOGY
ENVIRONMENTAL IMPACT STATEMENT

Figure 2. Environmental assessment and other environmental programs.

Table 5. Uses of outputs from the phased environmental assessment

- Input to supported EPA programs.
- Information necessary to undertake requisite control technology and health effects studies.
- Can be used to prepare an environmental impact statement.

Since the sampling and analytical procedures are optimized for each pollutant class and for each process, specific approaches cannot be described in detail. However, several manuals are being issued by the Process Measurements Branch which describe sampling and analytical options for level 2 sampling and analysis (refs. 2,3,4). In addition to the optimized sampling and analytical procedures which are used, sufficient samples must be obtained for bioassay (500 mg). To acquire such a sample size, level 1 procedures may have to be used.

The specific data which are generated by the phased environmental assessment can be used as shown in table 5. The relationship between environmental assessment and other environmental programs is shown in figure 2.

Conclusions

1. The phased approach to testing is more cost effective than alternative schemes.

2. Each phase of the environmental assessment yields information concerning the environmental insult associated with an energy related technology. The primary differences are cost, accuracy, specificity, and completeness of the analysis, and representativeness of the sample.

3. If the equivalent of level 1 information exists, then the researcher can prioritize the process streams and proceed directly to level 2.

REFERENCES

1. J. W. Hamersma and S. L. Reynolds, "Environmental Assessment Sampling and Analytical Strategies and Test Sampling and Analytical Costs," draft report, Oct. 1975.
2. Procedures for Process Measurements: Trace Inorganic Materials, TRW Systems Inc., July 1975.
3. P. W. Jones et al., "Analytical Methodology for Organic Industrial Effluents," draft report, September 1975.
4. W. Fairheller et al., "Sampling Techniques for Organic Industrial Effluents," draft report, August 1975.

SAMPLING PROCEDURES FOR PROCESS STREAMS

C. A. Flegal and J. W. Hamersma*

Abstract

This paper examines the application of two different approaches to the sampling of processes for environmental assessment. The approaches are illustrated for a specific type of coal gasification complex. These include a direct sampling approach in which all sampling and other necessary information is obtained in a single comprehensive effort and a phased approach where the same level of information is obtained in a two-step effort of varying aims and complexity. The requirements of these approaches in terms of sampling methodologies are discussed in detail with emphasis placed on two-step phased approach.

The current energy shortage and the emphasis on the use of energy with minimal environmental impact will result in the development of a large-scale new synthetic fuels industry based on coal conversion, oil shale processing, and biomass conversion. These new technologies will by nature of both their size and numbers have an impact on the environment. In addition, the environmental impact assessment of existing industries is becoming increasingly important. EPA is actively improving environmental assessment methodologies and prioritizing both the technical and economic requirements for these efforts.

A broad range of components that may be of environmental concern are being considered for environmental assessments of synthetic fuels processes such as a coal gasification complex. These components range from the primary gaseous products of carbon monoxide and hydrogen to the extremely high boiling polynuclear organic compounds (POM) as well as the entire range of inorganic species (refs. 1,2). A partial group of items of interest is shown in table 1. Biological response screening tests are also of interest.

Two sampling and analytical approaches (the phased and direct approaches) designed to give the same level of information for decisionmaking have been evaluated (ref. 3). The philosophy, information, benefits, and cost implications of each strategy were presented in detail in the previous paper.

The phased approach requires two separate levels of sampling and analytical effort to perform a complete environmental assessment. The first level of sampling and analysis has as its goal the identification of the pollution potential of a source in a qualitative and/or semiquantitative manner. This is done because at the initiation of an environmental assessment, little is known about the specific sampling requirements of a source both practically and technically. Thus, the first level utilizes qualitative and/or semiquantitative sampling and analysis procedures, identifies problem areas and allows the elimination of certain streams, components and classes of materials from further consideration in the overall assessment. Physical and biotesting is of a qualitative and survey nature consistent with the characteristics of the sample.

The second level sampling and analysis effort after having been focused by level 1 is designed to provide information that will resolve the questions or data gaps identified in level 1. Level 2 sampling and analysis will provide definitive data that will allow the environmental assessment of a source to be established. In order to perform this in a timely and cost-effective manner, the basic questions to be answered and major problem areas must already have been defined in level 1. Consequently, level 2 sampling and analysis is characterized by obtaining representative samples, accurate stream flow rates and by identification and quantification of specific organic and inorganic chemical classes and individual species. In this effort, biotesting in selected areas is expanded to include dose response data and also carcinogenicity testing.

The level 1 and level 2 sampling and analysis efforts are intimately linked in the overall environmental assessment effort. Level 1 develops and focuses the questions that must be answered by level 2. For example, if a level 1 test showed the presence of three to seven ring aromatics (PNA), level 2 sampling and analysis would be designed to determine the exact quantities of organics, the percentage of PNA, and the identity of as many specific PNA as possible (ref. 3). The results of this effort will provide sufficient information in the areas of physical characteristics, organic and inorganic chemical species characterization, and biochemical assaying such that stream control priorities and an initial estimate of process/control system regions of overlap can be established.

In this paper, the various sampling procedures for environmental assessments will be quickly reviewed for level 1 and level 2 requirements. In addition, a newly designed flue gas sampling system will be presented.

The Lurgi Coal Gasification Complex proposed by the El Paso Natural Gas Company for New Mexico was chosen as a somewhat typical coal conversion process for

---

*The authors are with TRW Systems, Redondo Beach, California.

Preceding page blank

Table 1. Some gasification product and byproduct species of interest

Component	Class	Item or Property of Interest
Gases	Inorganic	N_2, CO, O_2, H_2, Ar, NH_3, H_2O
	Acid Gases	H_2S, CO_2, SO_x, NO_x, HF, HCl, HCN
	Organic	CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10}, C_4H_8
	Sulfurous	COS, CS_2, CH_3SH, C_2H_5SH
Organic Liquids and Solids	Hydrocarbons	$C_5 - C_{12}$ hydrocarbons, benzene, toluene, xylene, indenes, naphthalenes
	Polynuclear Aromatic Compounds	pyrenes, fluoranthenes, phenanthrenes, fluorenes, acenaphthenes, benzopyrenes, chrysenes coronene
	Nitrogen Compounds	pyridine, picolines, lutidines, quinoline, isoquinoline, quinaldine, indole, carbazole, acridine
	Phenols	phenol, cresols, xylenols, naphthols
	Sulfur Compounds	mercaptans (thioalcohols), thiophenol, thiocresol, benzothiophene
Trace Elements	Nonvolatile	Ba, Be, Ca, Cr, Cu, Mn, Mo, Ni, Sr, V, Zn
	Volatile	As, B, Cd, F, Hg, Pb, Sb, Se, Sn
Coal, Ash, and Particulate	Ultimate	C, H, N, S, Cl, O
	Proximate	moisture, heat content, ash, volatiles, fixed carbon
	Sulfur Forms	total, pyritic, sulfate, sulfide
	Ash (Particulate)	SiO_2, Al_2O_3, Fe_2O_3, TiO_2, P_2O_5, CuO, CaO, MgO, Na_2O, K_2O, F, $SO_4^{=}$
Water	Dissolved Gases Organics Trace Elements	} See items listed above
	Ions	$S^{=}$, $SO_4^{=}$, NO_3^-, F^-, Cl^-, Br^-, CN^-, $PO_4^{\equiv}$, $CO_3^{=}$, HCO_3^-, SCN^-, H^+
	Gross Characteristics	BOD, COD, TOC, suspended solids, oil and grease, specific conductance

purposes of planning and analyzing environmental assessment strategies and requirements. The various sampling locations are shown superimposed on a model of the El Paso Plant in figure 1. A generalized flow scheme for sampling purposes has been simplified for quick reference use into the single block diagram in figure 2 which shows input and output streams only (refs. 1,2,4,5).

In the coal gasification complex, with the exception of the stacks and possibly the solids and slurry streams, there are generally little or no differences between level 1 and level 2 sampling locations. This is due to the fact that the predominant number of streams are homogeneous throughout the length of their respective transfer systems and since most samples are of the grab or composite type on both levels 1 and 2, the area of sample withdrawal need not change. However, sampling techniques will be different for levels 1and 2 (ref. 3).

The basic sampling strategy (figure 3) has been organized around the six general types of samples found in coal gasification or other complex process technologies rather than around the analytical procedures that will be required on the collected samples. The six sample types are delineated below:

- *Solids and solid slurries.* These are the coal input, bottom ash, and any aqueous stream containing more than 5 to 10 percent solids.
- *Liquid streams*
    - *Aqueous*. Water streams containing less than 5 to 10 percent insoluble solids.
    - *Nonaqueous*. Homogeneous streams other than water streams (usually organic).
- *Gaseous streams (containing no significant particulate)*. These samples include process streams, process vents, and ambient air samples.
- *Flue gas containing particulate*
- *Flue gas without particulate*. These streams are essentially the same as the gas streams except special procedures are used to sample for acid gases and PAH compounds.
- *Fugitive Dust Sampling*. This includes local source sampling and plant perimeter sampling employing high volume sampler techniques.

An examination of error analysis techniques make it apparent that if one particular error source has a much larger error than the other sources, the system error is very close to the largest single error. For this reason, it is logical to select sampling and analysis procedures for both levels that yield results of comparable accuracy. In the phased approach, the selection of sampling points and analysis techniques relies on the concept that level 1 sampling is oriented towards obtaining survey and/or semiquantitative results only, whereas level 2 sampling and analysis is intended to acquire more accurately the data necessary to perform an environmental assessment. Consequently, a level 1 sample may be taken from any easily accessible port within the flow scheme of a given unit. For example, in obtaining a level 1 stack sample, the probe may be inserted in any convenient location along the duct leading to the stack and a pseudo-isokinetic sample may be taken in order to obtain qualitative data. On level 2, however, where quantitative data are required, isokinetic samples must be withdrawn from specific locations away from ducting bends and other obstructions in order to ensure a more quantitative sample. Stream parameters such as flow rates, temperature, pressure, and other physical characteristics will be obtained on both levels within the accuracy requirements of a given level of sampling. Application of these concepts to sampling a coal gasifier is shown in figure 3.

In the phased and direct sampling efforts for the gasifier, many effluent parameters must be determined onsite due to their unstable nature and it is assumed that most other large-scale plants will have similar samples. Mobile laboratories in the form of vans or trailers are recommended for source assessment efforts such as stack sampling, ambient air sampling and water quality measurements. In general, commercially available vans have been outfitted with a variety of equipment necessary for assessing environmentally significant factors for the source of interest.

The sampling procedures to be employed for solid materials are quite varied and must be tailored to the stream being sampled. Sites vary from large piles of material, contained solid piles such as in hoppers, silos or vehicles and flowing systems as in pneumatically driven flowing streams, process streams, or conveyor systems. The most important factor in the choice of the sampling device is to obtain a truly representative sample.

The extremely wide variety of situations requiring sampling makes it difficult to specify exactly what method should be used or what equipment manufacturers should be specified. Level 1 sampling program should employ simple procedures that will provide sufficiently representative sample in a short time period. This sample can often be a simple grab sample, taken at one time. If the site to be sampled is a pile of material, equal portions at random locations can be removed, combined, coned, and quartered. If the sample is to be taken from a conveyor or elevator, the device could be stopped and a sample removed over the complete width and depth of the stream. This is essential so that all size particles be sampled as size segregation does occur in such a moving system. If the device is a moving sample in an enclosed duct or pipe, then a cutter to separate a portion of the stream can be employed.

In level 2 and control device development sampling

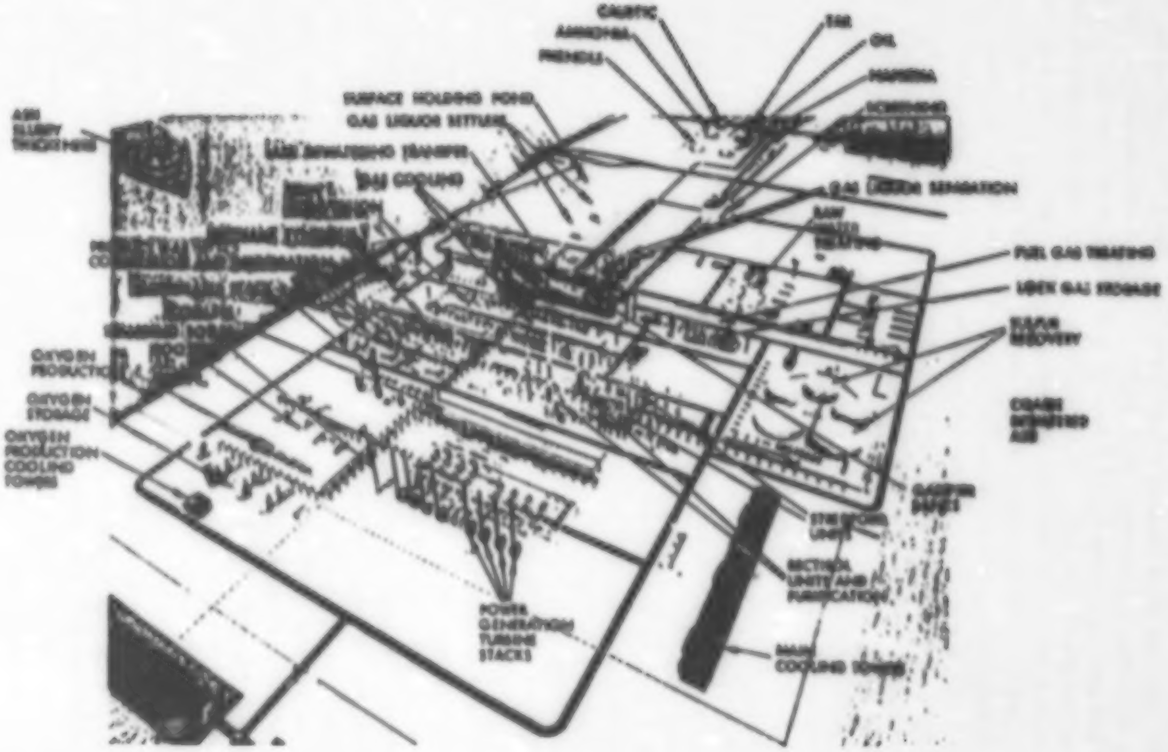

CAUSTIC
AMMONIA
PHENOLS
TAR
OIL
NAPHTHA
SURFACE HOLDING POND
GAS LIQUOR SETTLING
GAS COOLING
ASH SLURRY THICKENERS
FUEL GAS TREATING
SULFUR RECOVERY
OXYGEN PRODUCTION
OXYGEN STORAGE
OXYGEN PRODUCTION COOLING TOWERS
POWER GENERATION TURBINE STACKS
STRETFORD UNITS
MAIN COOLING TOWERS

Figure 1. Model of El Paso Lurgi coal gasification complex
(total area – 1.5 sq. mi.)

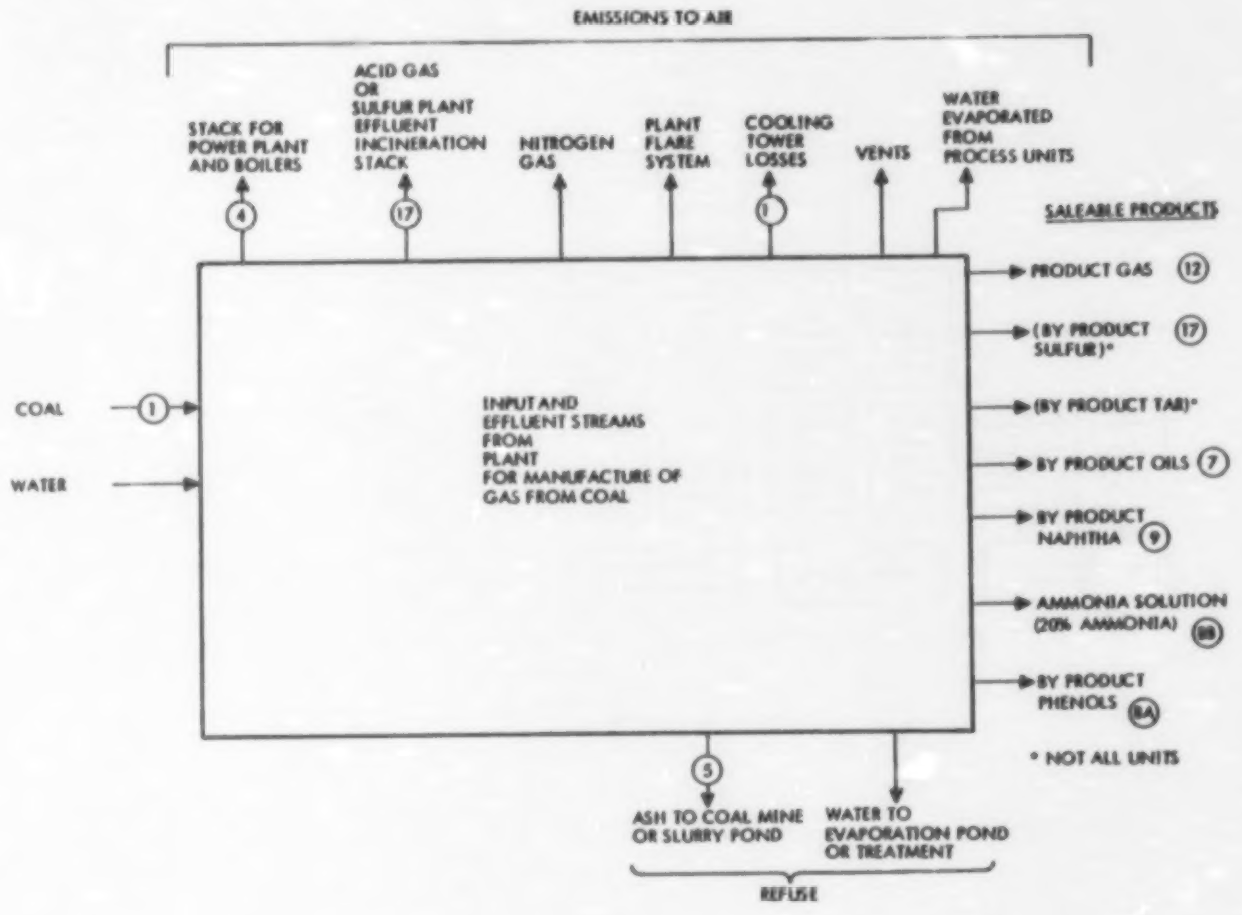

EMISSIONS TO AIR
STACK FOR POWER PLANT AND BOILERS
④
ACID GAS OR SULFUR PLANT EFFLUENT INCINERATION STACK
⑰
NITROGEN GAS
PLANT FLARE SYSTEM
COOLING TOWER LOSSES
①
VENTS
WATER EVAPORATED FROM PROCESS UNITS
SALEABLE PRODUCTS
PRODUCT GAS ⑫
(BY PRODUCT SULFUR)* ⑰
(BY PRODUCT TAR)*
BY PRODUCT OILS ⑦
BY PRODUCT NAPHTHA ⑨
AMMONIA SOLUTION (20% AMMONIA) (8B)
BY PRODUCT PHENOLS (8A)
* NOT ALL UNITS
COAL
①
WATER
INPUT AND EFFLUENT STREAMS FROM PLANT FOR MANUFACTURE OF GAS FROM COAL
⑤
ASH TO COAL MINE OR SLURRY POND
WATER TO EVAPORATION POND OR TREATMENT
REFUSE

Figure 2. Gasification plant effluent flow diagram.

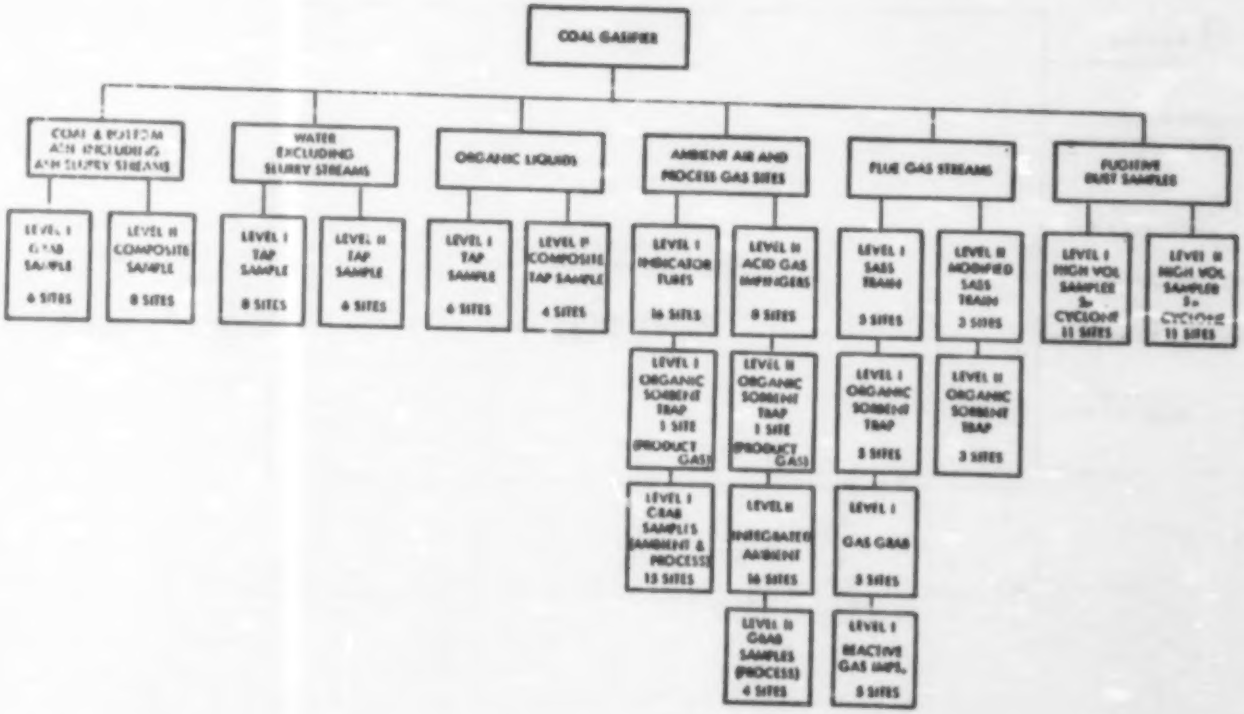

COAL GASIFIER
COAL & BOTTOM ASH INCLUDING ASH SLURRY STREAMS
LEVEL I GRAB SAMPLE 6 SITES
LEVEL II COMPOSITE SAMPLE 8 SITES
WATER EXCLUDING SLURRY STREAMS
LEVEL I TAP SAMPLE 8 SITES
LEVEL II TAP SAMPLE 6 SITES
ORGANIC LIQUIDS
LEVEL I TAP SAMPLE 6 SITES
LEVEL II COMPOSITE TAP SAMPLE 4 SITES
AMBIENT AIR AND PROCESS GAS SITES
LEVEL I INDICATOR TUBES 16 SITES
LEVEL I ORGANIC SORBENT TRAP 1 SITE (PRODUCT GAS)
LEVEL I GRAB SAMPLES (AMBIENT & PROCESS) 13 SITES
LEVEL II ACID GAS IMPINGERS 8 SITES
LEVEL II ORGANIC SORBENT TRAP 1 SITE (PRODUCT GAS)
LEVEL II INTEGRATED AMBIENT 16 SITES
LEVEL II GRAB SAMPLES (PROCESS) 4 SITES
FLUE GAS STREAMS
LEVEL I SASS TRAIN 3 SITES
LEVEL I ORGANIC SORBENT TRAP 3 SITES
LEVEL I GAS GRAB 3 SITES
LEVEL I REACTIVE GAS IMPS. 3 SITES
LEVEL II MODIFIED SASS TRAIN 3 SITES
LEVEL II ORGANIC SORBENT TRAP 3 SITES
FUGITIVE DUST SAMPLES
LEVEL I HIGH VOL SAMPLER & CYCLONE 11 SITES
LEVEL II HIGH VOL SAMPLER & CYCLONE 11 SITES

Figure 3. Coal gasifier – sampling site survey chart.

programs, the procedures should provide an accurate integrated sample. Samples of piles or hopper contained material should be obtained using a pipe borer, slotted tube (thief) or auger samplers that can reach from the top to the bottom of the material. The choice of the device will largely depend on the physical condition such as moisture content, particle size and degree of agglomeration of the material. The locations of the sample sites within the material should follow a specific pattern so that each area of the material can be sampled. Moving streams should be sampled in one of two ways. One is to use a riffler or whistle pipe which removes a portion of the stream continuously. The other method is remove a portion of the complete stream at specific time intervals. Numerous devices of this type have been designed that involve cutters, scrapers, swinging arc samplers, etc. The most important consideration is that the entire cross-section of the stream by sampled and that the sample be removed at the stream velocity (refs. 1,6).

Procedures for sampling aqueous streams are well established and many suitable procedures are available. Some of these procedures are based on chemical analysis of specific components for analysis and biological effect evaluation and should be chosen for the specific application (ref. 3). The organic content of an aqueous stream can vary widely in composition and nature. Low molecular weight polar compounds may be water soluble. High molecular weight material may be insoluble and thus result in a two-phase nonhomogeneous system. The non-homogeneous streams tend to be stratified and thus make the sampling job more difficult. Composite sampling with a multi-point probe system is the most convenient method to obtain a truly representative sample. If the stream is homogeneous, then single point probes on the sampler are sufficient (refs. 1,6).

At the present time, there is a number of suitable single point and multipoint sampling devices on the market. Sampling can be for a single or very short time period, essentially a grab sample, a long term composite sample or individual samples obtained by a sequential sampler. The choice largely depends on the reason for the sample and the available time. For level 1 studies, a one time sample should suffice, while for level 2 sampling, it is recommended that the composite type or the sequential sampler be employed. The latter device yields separate samples which can be analyzed individually or composited as desired.

Nonaqueous samples will be primarily organic in nature with little or no inorganic constitutents. In the El Paso Natural Gas plant, a portion of the raw coal input into the gasifier (4 to 8 percent) is converted into a variety of liquid organic byproducts, ranging from low boiling napths to extremely high molecular weight tars and tar solids. Many of the sampling procedures for aqueous streams are applicable for other liquid streams as well. This sampling has been practiced for a considerable time by the petrochemical industry, and has been adequately specified by ASTM and API Standards D 270 and 2546, respectively (ref. 7). If automatic samplers are available for the streams in question, they should be used in accordance with the plant sampling schedule as a first preference.

When selecting a method for sampling aqueous liquid streams, it is important to keep in mind the nature of the stream and the purpose for which it will be analyzed. For example, samples of low viscosity and boiling point such as naphtha, light oil, and ammonia do not stratify or precipitate solids. Thus, it is very likely that a single grab sample will be sufficient. On the other hand, tar and heavy oils are viscous materials that can stratify and precipitate solids when cooling. In these cases, care must be exercised to take a hot sample and use a more elaborate method that avoids sampling only one part of a stratified stream. In addition, it should be remembered that pure streams or streams with a narrow boiling point range are much easier to sample than a stream that contains naphtha through tar.

Fugitive dust sampling will definitely be a consideration for coal conversion processes. The sampling and analysis of dust in areas utilizing large quantities of coal and ash establishes an overall ambient particulate concentration profile. The primary consideration in boundary sampling involves positioning the high volume air samplers in such a way that samples representative of the overall atmosphere are obtained. One way of doing this is to place four samplers equidistantly at 90° angles to each other in order to account for fluctuations in wind intensity and direction. Samples taken over a one week period will provide additional information in establishing an accurate data profile (refs. 3,8,9).

There are several types of gas sampling requirements in coal gasification systems. These include:

- Process streams, effluents, and vents
- Ambient air samples
- Flue gas
- Gasifier output.

Gas sampling methods utilize either a grab sampling apparatus or an integrated air sampling apparatus. One grab sampling and integrated air sampling system undergoing development utilizes an in-line silica gel absorption tube for the purpose of trapping reactive constituents (acid gases and particulates) which might otherwise alter the sample composition by chemical reaction and/or sorption.

Ambient air samples are taken to assess the extent of the problem by determining the overall plant contribution of toxicants to the atmosphere. The primary objective in obtaining this type of sample is to ensure that the atmosphere sampled consists of a representative segment of the process environment. This is best accomplished by establishing a profile derived from the simultaneous operation of four integrated sampling units placed equidistantly from one another in the same manner as for fugitive dusts.

Obtaining a representative sample of the effluent from process power plant and incinerator stacks is a complex task, since all process parameters vary with both time and location within the stack. Consideration must be given to a variety of factors, such as flow rate, sampling time, changes in loading (attributable to cyclic process changes), and suitable impingement techniques needed to entrain the various components of interest (table 1) (refs. 9,10,11). In the Lurgi system, the power plant and acid gas incinerator stacks (streams 7 and 13 of figure 2) will also need to be sampled.

Recently, a new train for sampling flue gases for environmental assessments has been designed and tested. The project was an integral aspect of an overall EPA program to acquire a variety of industrial flue gas particulate samples in sufficient quantity to permit evaluation of comprehensive biological and chemical testing methodology for environmental assessments. In the project, the utility of a prototype series cyclone sampling train was carefully evaluated. The train was fabricated and calibrated by TRW based on a Southern Research Institute cyclone design and utilizing an Aerotherm Corporation high volume stack sampler (all designed under EPA funding). The train (figure 4) was composed of three cyclones designed to provide large quantities of particulate matter, size classified in the ranges of (a) $>10\mu$, (b) 3μ to 10μ, and (c) 1μ to 3μ. A final filter to provide a submicron size cut and a commercial high volume stack sampler pump and control system (Aerotherm HVSS) completed the system (ref. 11).

The primary objectives of this program were to acquire the particulate emission samples from eight to ten industrial sources utilizing the newly designed series cyclone train and to disburse sample aliquots to participating agencies and contractors for the following tests:

- Cytotoxicity
- Mutagenicity
- Spark Source Mass Spectrometry
- High Resolution Mass Spectrometry
- Gas Chromatography/Mass Spectrometry and/or
- Others as directed by EPA.

Mitre Corporation functioned as project coordinator for EPA and the results are presented in a separate paper.

The probes, transform, cyclones and interconnect lines were fabricated exclusively from 316 CRES stainless steel. This alloy was extensively tested and found to be nontoxic and non-inhibitory in biological compatibility testing on TRW's Viking Lander Biology Instrument program to test for life on Mars conducted for NASA. The probe, transform and 10μ cyclone had thermocouples placed as shown in figure 4 and were heat wrapped and insulated.

The 3μ and 1μ cyclones and Aerotherm filter housing were installed in the standard Aerotherm HVSS oven. The filter material chosen by EPA for use was a Teflon needle felt material pretested and found acceptable for cytotoxicological purposes. The standard glass fiber filter material stipulated for the EPA Method 5 train was found to cause an interference in the biological testing.

One of the major concerns of the project was that sample integrity must be maintained, i.e., cross-contamination between samples and spurious external contamination from "dirty" brushes, spatulas, bottles, the environment, etc., must be prevented. It was essential that a valid correlation be possible between cytotoxicity or mutagenicity and the trace chemical composition of the sample and possibly the general type of process. Toward this goal, all equipment that would contact the samples (nozzle, probes, cyclones, interconnect tubing, fittings, filter housings, bottles, brushes, spatulas, petri dishes, etc.) were cleaned, inspected and packaged per TRW procedures demonstrated under the VLBI Program to preclude potentially toxic contaminants from the samples.

Flue gas sampling procedures for organic components are currently in the research and development stage. Organic emissions occur in the condensed, readily condensible and gaseous forms. Of these, the gaseous forms present a serious challenge to the design of efficient sampling and concentration approaches. In general, the condensed organic species can be removed by filtration of an integrated sample over a period of time sufficient to satisfy the detection limit of the analytical procedure. Similarly, readily condensed species can be sampled employing trapping procedures at ice or dry-ice temperatures with care taken to avoid loss of material by microfog (submicron aerosol) formation.

The detection and quantitative measurement of trace organic vapor species generally requires a concentration step to attain the required detection limits. The most frequently employed concentration techniques are solvent scrubbing, condensation (cryogenic trapping), adsorption on activated carbon, chromatographic equilibration, chemical reactions, and chromatographic column trapping. Potentially, the most attractive

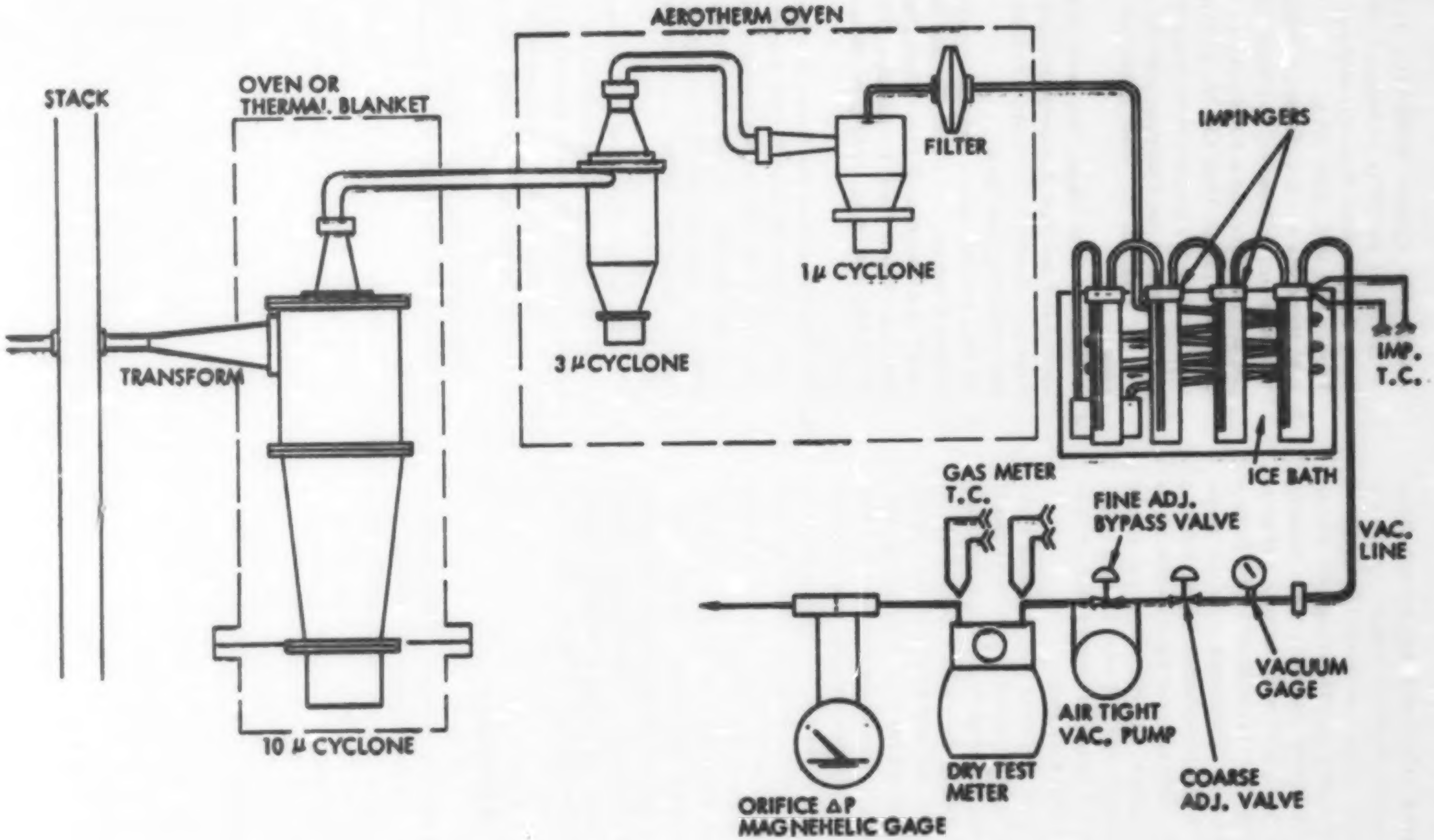

STACK
OVEN OR
THERMAL BLANKET
TRANSFORM
10 µ CYCLONE
AEROTHERM OVEN
3 µ CYCLONE
1 µ CYCLONE
FILTER
IMPINGERS
IMP.
T.C.
ICE BATH
VAC.
LINE
GAS METER
T.C.
FINE ADJ.
BYPASS VALVE
VACUUM
GAGE
AIR TIGHT
VAC. PUMP
COARSE
ADJ. VALVE
DRY TEST
METER
ORIFICE ΔP
MAGNEHELIC GAGE

Figure 4. Schematic of series cyclone stack sampling train.

method for collecting and concentrating organic substances from ambient air or stationary emission sources employs the adsorption and/or partitioning properties of materials normally used in gas chromatographic analysis to retain organic substances selectively while removing the major diluent gases, such as air, nitrogen and water vapor. The porous polymer materials are used in particulate laden streams as a supplemental collection media following a filter or cyclone collection device. Standard Method 5 systems have been used for collection of the particulate in the probe and filters and the volatile organics in the impinger liquid. A more efficient procedure is to employ the porous polymer in place of or in addition to the impinger collection.

The possibility of employing the inorganic multicyclone approach for both organic and inorganic sampling is currently being explored. Aerotherm Corporation is currently repackaging the cyclone train described earlier to reduce the size and weight of the cyclone system, to provide the capability of sampling high temperature systems and to incorporate organic vapor traps. The system, with the enlarged adsorber, should be capable of collecting both organic and inorganic samples at the same time. At 5 scfm, sampling times should be about one hour to obtain sufficient material for both level 1 chemical analysis and biological testing. The probe, cyclone and filter collected material would be analyzed for both organic and inorganic constituents, as would the adsorber, and the condensed trap. This system will be tested in 1976 on the Combustion Power Company CPU-400 test facility during an ERDA funded test of the coal-fired combined cycle potential of the system.

REFERENCES

1. J. W. Hamersma and S. L. Reynolds, "Tentative Procedures for Sampling and Analysis of Coal Gasification Processes," EPA Contract 68-02-1412, Task No. 3. (Prepared for the Office of Research and Development, Environmental Protection Agency, Research Triangle Park, N. C., March 1975).
2. J. W. Hamersma and S. L. Reynolds, "Review of Process Measurements for Coal Gasification Processes," EPA Contract 68-02-1412, Task No. 3. (Prepared for the Office of Research and Development, Environmental Protection Agency, Research Triangle Park, N. C., April 1975).
3. J. W. Hamersma and S. L. Reynolds, "Environmental Assessment of Sampling and Analytical Strategies and Test Sampling and Analytical Costs," EPA Contract No. 68-02-1412, Task No. 9. (Prepared for the Industrial and Environmental Research Laboratory, Environmental Protection Agency, Research Triangle Park, N. C., Draft Submitted October 1975).
4. H. Shaw and E. M. Magee, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes," Gasification; Section 1, Lurgi Process, EPA-650/2-74-009-C, July 1974.
5. "El Paso Natural Gas Company Burnham Coal Gasification Complex-Plant Description and Cost Estimate," Application of El Paso Natural Gas Co. Before U.S. Federal Power Commission, Docket No. CP 73-131, August 16, 1972 (Rev. September 20, 1972).
6. "Approved Procedures for Process Measurements – Trace Inorganic Materials," TRW Systems Group, EPA Contract No. 68-02-1393, February 1975.
7. "Standard Method of Sampling Petroleum and Petroleum Products," ASTM Committee D-2, 1971 Annual Book of ASTM Standards, Part 18, D270-65, 47-71.
8. "Planning the Sampling of the Atmosphere," ASTM Committee D-22, 1971 Annual Book of ASTM Standards, Part 23, D1357-57, 291-297.
9. D. L. Brenchley C. D. Turley, and R. G. Yaime, "Industrial Source Sampling," Ann Arbor Science, Ann Arbor, Michigan, 1973.
10. "Air Sampling Instruments," American Conference of Governmental Industrial Hygienists, 4th Edition, 1972.
11. T. Chamberlain, D. Jones, J. Trost, and A. Grant, "Fabrication and Calibration of a Series Cyclone Sampling Train," EPA Contract No. 68-02-1412, Task No. 7. (Prepared for the Office of Research and Development, Environmental Protection Agency, Research Triangle Park, N. C., April 1975).

ANALYTICAL TECHNIQUES FOR SAMPLE CHARACTERIZATION IN ENVIRONMENTAL ASSESSMENT PROGRAMS

C. H. Lochmüller*

Abstract

A tiered approach to chemical analysis in an environmental assessment program can be both the most cost effective and information effective strategy. On the other hand, a tiered approach requires the development of a more general scheme for analysis than would a potentially more costly direct, single-phase program.

In a tiered approach, the first level of analytical effort is a standardized inorganic/organic scheme applied to all samples collected at the site to be assessed. The second tier analytical effort, however, is optimized for a given sample type and requires a great deal more professional judgment and flexibility in its application. This paper discusses methods of choice, criteria for selection, analysis costs and report contents for an analytical effort which could be applied to a tiered environmental assessment program.

INTRODUCTION

The modern analytical chemist has at his disposal a veritable arsenal of sophisticated techniques applicable to the task of sample characterization. Given unlimited resources, each of these techniques could be applied in turn to every sample taken from a process feedstock, waste or product stream. Where resources are finite, it is the analyst's first obligation to devise an analysis strategy which is both cost and information effective. Two extremes are immediately apparent: (1) direct analysis of each sample for all its components, or (2) direct analysis for a limited list of known hazardous materials. The former approach would be highly information effective but very costly; the latter, certainly inexpensive but does not provide information about unsuspected substances which might be hazardous but are not included in the list and for which there are no analyses.

An intermediate strategy is a tiered or phased approach in which analysis occurs at three levels of investigation. The Level I scheme is a general one which includes physical characterization (e.g., particle size and morphology), inorganic and organic chemical analysis and bioassay for cytotoxicity and mutagenicity. It was designed to give maximum cost and information effectiveness and have a broad range of applicability. The information from this phase is used to prioritize the various streams in rank order of their potential environmental hazard and to plan an optimized sampling and analysis strategy for those streams where a hazard exists. Execution of this latter strategy is Level II of the tiered approach. In some cases, a further refinement may be necessary after Level II, e.g., isolation and identification of a particular chemical species from within a given class. Level III seems to follow certain key materials over the extremes of process variation by providing continuous analysis methods. This paper attempts to show the elements of the overall strategy of a phased analytical approach with special emphasis on the component parts of the generally applicable first phase, or Level I, scheme. Included are some actual results obtained both in-house at the Industrial Environmental Research Laboratory, Research Triangle Park (IERL/RTP) and externally in the laboratory of a Process Measurements Branch contractor.

THREE-TIERED ANALYSIS SCHEME

In general, the methods to be described will be applied in laboratories that are remote to the process sampling site. As has been previously discussed (viz. Statnick), certain volatile or unstable substances are best analyzed for onsite by techniques such as gas chromatography. The majority of the analyses are done in remote laboratories because of the need for skilled technical personnel, special operation conditions and primarily because of the higher cost-effectiveness of this approach.

A flow chart of the Level I analytical scheme (fig. 1) shows the various components of the overall scheme and their interrelationships. The basic divisions are: (1) physical, (2) chemical and, (3) bioassay. Chemical analysis is subdivided into separate schemes for inorganic and organic components. The bioassay procedure includes *in vitro* test procedures, e.g., cytotoxicity or mutagenicity.

PHYSICAL CHARACTERIZATION OF SOLIDS – LEVEL I

Level I physical characterization is inexpensive and, in most cases, nondestructive. In flue and stack gas samples, particle size distribution information is provided by

---

*The author is on leave to the U.S. Environmental Protection Agency, Research Triangle Park, N.C., from Duke University where he is an Associate Professor of Chemistry.

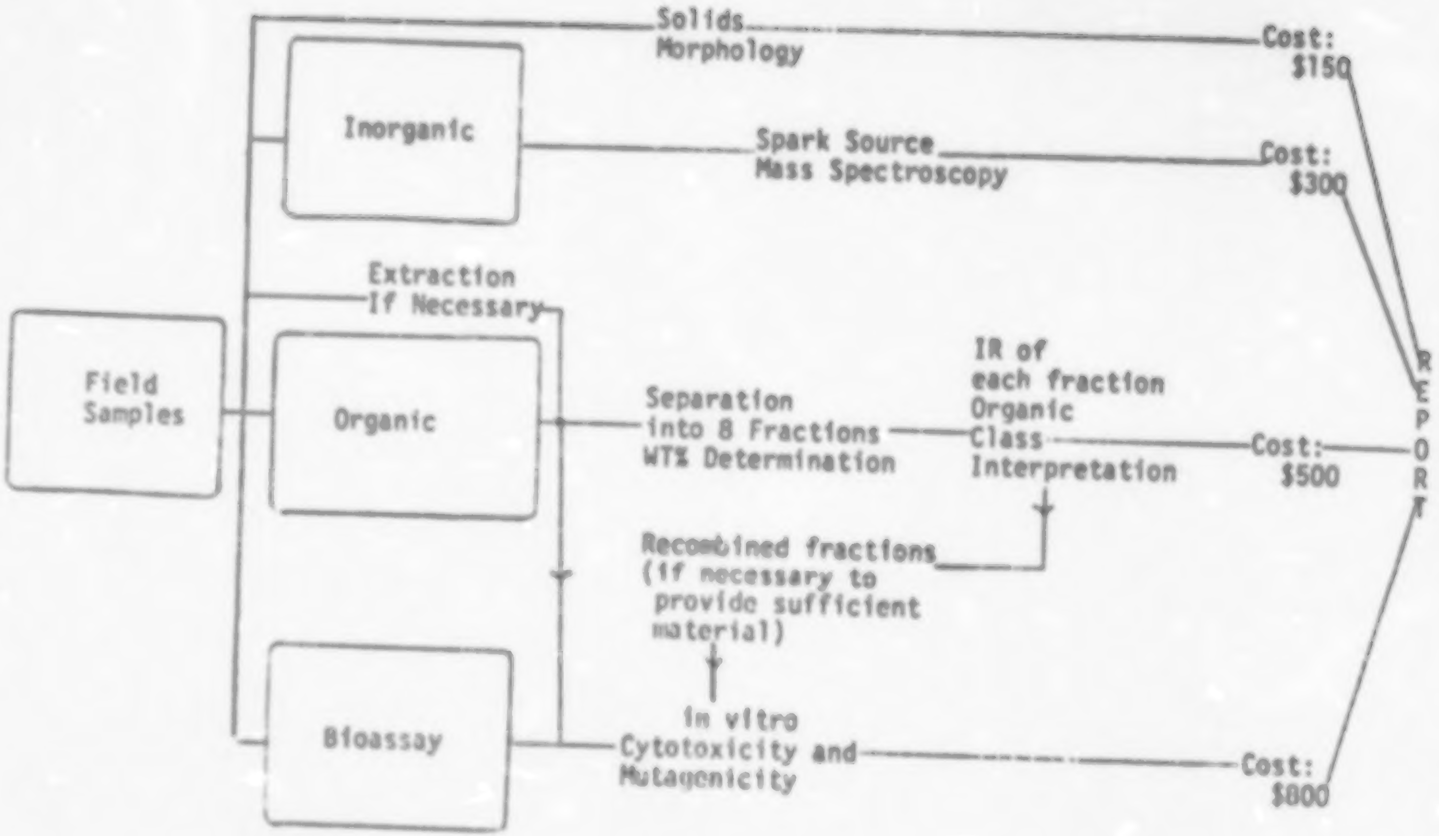

Field Samples
Inorganic
Organic
Bioassay
Solids Morphology
Spark Source Mass Spectroscopy
Extraction If Necessary
Separation into 8 Fractions WT% Determination
IR of each fraction Organic Class Interpretation
Recombined fractions (if necessary to provide sufficient material)
in vitro Cytotoxicity and Mutagenicity
Cost: $150
Cost: $300
Cost: $500
Cost: $800
REPORT

Figure 1. Flow chart of level 1: environmental assessment analysis scheme.

the "cut-point" (d_{50}) values of the series cyclones of the sampling train (i.e., 10, 3, 1μm respectively). For other solid samples, optical microscopy for gross morphology is one suitable technique and, in most cases, will detect distinctive substances such as asbestos. A photomicrographic record of the sample is both worthwhile and low cost. More sophisticated techniques such as scanning electron microscopy are considered too expensive for routine inclusion.

CHEMICAL ANALYSIS – LEVEL I

The intent of the chemical analysis scheme at this phase of assessment is to provide qualitative and quantitative information relevant to the element composition of process samples and the identity of the major classes of organic chemical compounds present.

INORGANIC ANALYSIS

Inorganic analysis at Level I utilizes the Spark-Source Mass Spectrometry (SSMS) technique to achieve qualitative and semiquantitative elemental analyses on all solids, particulates, filterable solids from liquid streams and the residues of evaporated liquid samples. This technique was selected from the many others available (e.g., atomic absorption, emission and x-ray fluorescence spectrometry and neutron activation analysis) because of its general multi-element capability, acceptable detection limits, speed and cost. Precision and accuracy of a factor of 2 and a detection limit of 1 ppm for elements analyzed are specified. Spark source mass spectrometric analysis for some 80 elements costs about $300 commercially including sample preparation. A comparison of SSMS and several other techniques can be found in table 1.

ORGANIC ANALYSIS

The objective of Level I organic analyses (table 2) is to achieve quantitative estimate of the predominant classes of organic compounds present in samples taken from process streams. Organic compounds are often described in terms of classes. This terminology has a very specific connotation. Classes of organic compounds include, for example, alcohols, ketones, aldehydes, caboxylic acids, amines, etc. While it is indeed possible to fractionate complex mixtures into classes, this is a difficult and costly procedure. At Level I, the strategy is to isolate well-defined fractions by conventional liquid chromatography. Under controlled conditions, the content of a chromatographic fraction (in terms of class types) is fairly predictable. An example of the relation between organic class and chromatographic fraction is illustrated in figure 2.

Organic extracts are resolved into eight fractions by liquid/solid chromatography on silica gel, utilizing a prescribed series of eight solvent mixtures as eluants. The fractions are evaporated to constant weight by methods that minimize evaporative loss of the constituents of interest. The weight of each fraction is determined to 0.1 percent or 10 g. As an aid to identification of the constituents of each fraction, an infrared adsorption spectrum is obtained and interpreted. Interpretation at this stage is in terms of classes which may be present. For the infrared analysis, a grating instrument covering the range 4,000-600 cm^{-1} is required. The total cost of a Level I organic analysis is estimated at $450, not including the infrared interpretation.

BIOLOGICAL ANALYSIS

The biological tests included in the Level I analysis scheme are intended to provide indications of potential biohazards independent of chemical analysis. This environmental assessment tool is an important aspect since chemical information, as mentioned earlier, is an ambiguous predictor of biological activity. Level I chemical analysis is a search for danger signals; bioassay provides additional indicators.

Like the chemical analysis, Level I bioanalysis must remain relatively simple and inexpensive. For this reason, only in vitro or "test tube" methods may be seriously considered part of the first level. The selected methods discussed in this section provide an estimation of acute toxicity and certain types of mutagenic activity. In addition to being of direct interest, mutagenic behavior is an effective screening indicator for carcinogenic activity. Although not all mutagens are carcinogenic, nearly all carcinogens cause mutagenesis.

An estimate of the acute toxicity could be determined by means of the rabbit alveola macrophage procedure. Although the system presents opportunities for considerably more sophisticated and subtle studies, only cell mortality at a single pollutant concentration, compared to controls, would be utilized as part of Level I.

Particulate samples are added—in weighed quantities, to the culture medium and incubated before adding the test cells. After a second incubation, the number of dead and living cells are determined by dye exclusion techniques. Water-immiscible liquid samples are treated identically except for the initial incubation period. Water-immiscible samples may be solubilized by treatment with dimethyl sulfoxide. Organics trapped by

Table 1. Comparison of analytical techniques

Technique	Multielement Capability	Accurary	Sensitivity
DC Arc/AC Spark (OES)	Unable to run Hg, Se, Sb or F	±30-50% semi quant. ±10% quant.	Generally acceptable varies with matrix
ICPOES	Unable to run F, additional elements up to 40 depends on instrument	~±40%	Acceptable
X-Ray Fluorescence (XRF)	Unable to run Li, Be or B	Qualitative to ±10% depending on element and matrix	Variable depends on element and matrix
Atomic Absorption Spectroscopy (AAS)	None	±10-<1% depending on concentration and standards	Acceptable, varies with element
Neutron Activation (NAA)	Be not done effectively F, Pb require special handling	±30% semi quant. ±2-3% quant.	Acceptable, varies with matrix
Spark Source Mass Spec (SSMS)	All elements can be determined	100-300% "quick and dirty" ±30% semi quant.	Acceptable
Isotope Dilution (SSMS)	Cannot do Hg, As, Be, Mn, F or Na	<5%	Acceptable

Table 2. Level 1 organic analysis

Compound	Compound Class	Fraction Contained	Identified as
n-octadecane	hydrocarbon	1	hydrocarbon
anthracene	aromatic	1,2	anthracene
	ester*	3,4	ester*
stearone	ketone	4	ketone
phenol	phenol	4,5	phenol
1-octanol	alcohol	5	1-octanol
5-diphenyl urea	urea (diamide, aromatic	6	aromatic amide
p-toluenesulfonic acid	alkylaryl sulfonic acid	7,8	alkyl benzene sulfonate (acid or salt)
octadecylamine	amine	(6)	amine
dimethylsulfoxide	sulfoxide	7	DMSO
suberic acid	carboxylic acid	n.f	n.i

*Suberic acid octylester formed in sample work-up from the acid, octanol and the presence of an aryl sulfonic acid

Note: underline indicates fraction containing major portion of material.

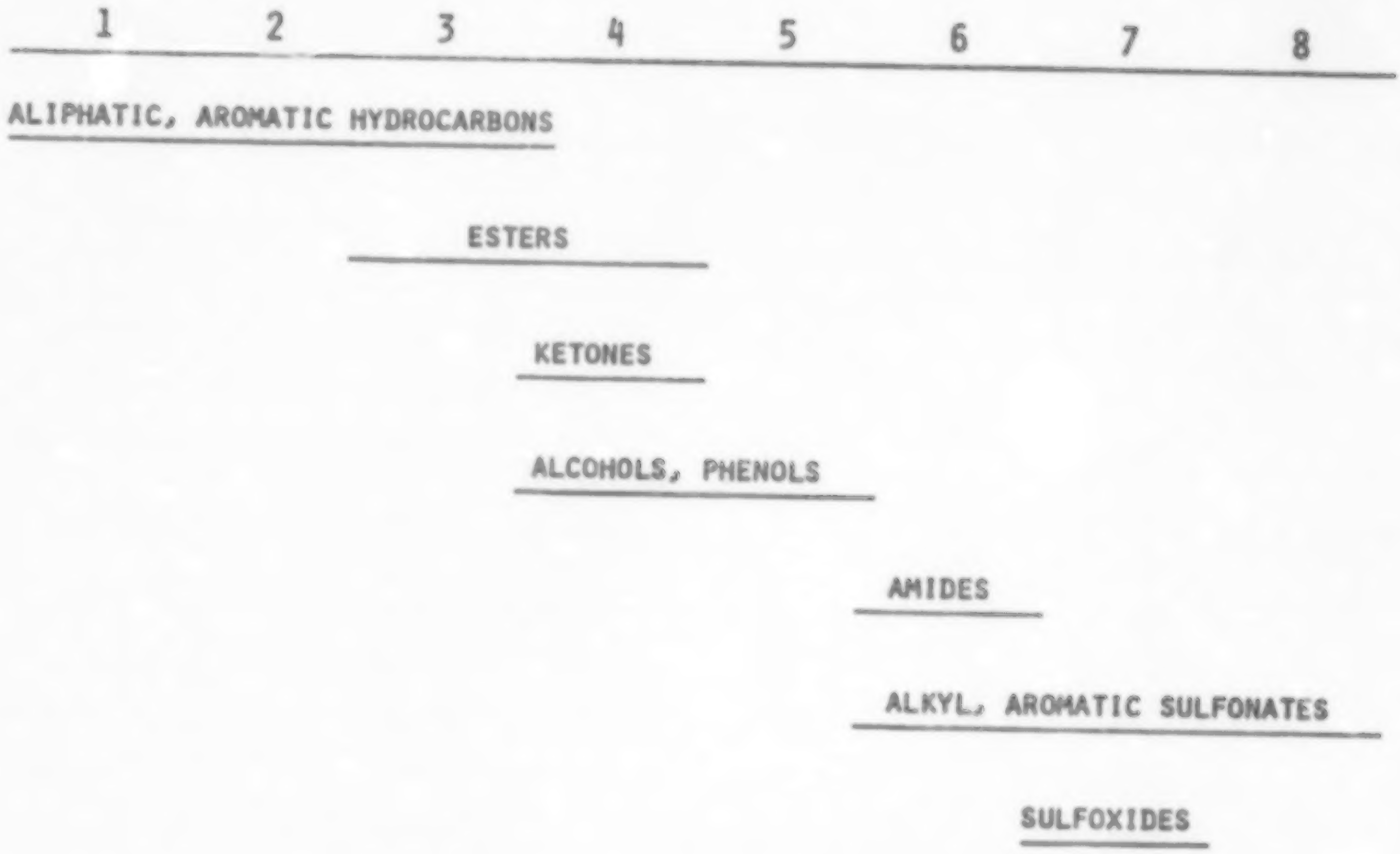


Figure 2. Liquid chromotographic fractions vs. class types.

porous polymer adsorbents are extracted with a compatible solvent (pentane in the case of Tenax-GC, ENKA, Holland), reduced in volume, and then taken up in dimethyl sulfoxide for addition to the test system.

The recommended test for mutagenesis is carried out using a B. Ames-type procedure with selected strains of micro-organisms. At Level I, only one concentration is tested and only one solvent system is employed. Dimethyl sulfoxide has been selected as the solvent most likely to give "worst case" results, a desirable goal at Level I.

Solid samples are dissolved as completely as possible in dimethyl sulfoxide, filtered, and added to the test system. Liquid samples are added to dimethyl sulfoxide and then to the test system.

Skilled technicians under close supervision of a professional cytologist and bacterial geneticist are required for the cytoxicity and mutagenicity testing, respectively. Laboratories must be well equipped and carefully managed to prevent chemical or biological contamination of samples and to avoid health hazards to the test personnel. Interpretation of results must be accomplished by experienced personnel. Therefore, this work would only be conducted in laboratories approved by EPA health effects programs. Estimated combined cost is $800.00 for cytotoxicity-mutagenicity testing.

CHEMICAL COMPONENTS OF LEVEL I IN PRACTICE

Of the chemical analysis procedures used in Level I, SSMS is the most straight-forward. It is tempting to list many of the analytical results we have achieved with this technique, but such lists would have little meaning without background information related to each source. More to the point of this paper are the data from some feedstock samples run "in-house" using both SSMS and NAA. As can be seen from table 1, the two methods are essentially equivalent within the errors involved for the elements analyzed. SSMS yielded more overall information without special effort.

The results of a Level I organic analysis on a synthetic sample prepared in our lab and run "blind" by our contractor is shown in table 3. As can be seen, the combination of liquid chromatography– infrared spectroscopy yielded a significant amount of specific as well as class information. Utilizing conventional infrared techniques, the limit of detection varied from 20-200 μg depending on the relative infrared sensitivity. Utilizing more advanced techniques such as Fourier Transform Infrared Spectroscopy, the limit of detection could be reduced 100-fold and more speciation information could be obtained at very little increased cost.

LEVEL II – Analysis Strategy

Level II analyses are carried out on streams that have been prioritized in Level I Environmental Assessment programs. It is not possible to present a chemical analysis strategy for Level II in the detail possible in Level I. In Level II, every problem is stream specific and will require individual planning. The techniques used include the entire "arsenal" referred to previously, but could be a more quantitative application of Level I methods, modifications of these or new techniques. What can be said is that Level II methods will either be *classification* or *speciation* techniques. The former identifies a particular compound type–e.g., oxide, phenolic, amine, etc., while the latter identifies a particular compound itself–e.g., PbO, m-bromophenol, aniline, etc. The latter will rarely be used and only in those cases where specific control devices must be implemented. The speciation techniques are often more expensive to execute because of the need to separate the material of interest from its matrix.

In Level II, bioassay is expanded to include "dose-response" measurements and tests for carcinogenicity. This further delineates the potential human hazard and the nature of the problem.

LEVEL III – Analysis Strategy

In Level III, the limits of process variation and its effect on certain "indicator" species, e.g., total sulfur for sulfur compounds, nondispersive IR for nitro compounds, are studied. In this phase, the long-term average, process-related environmental hazard is assessed. It is anticipated that at regular intervals, Level I or II methods will be used as a check on the significance of the continuous process-monitor results.

SUMMARY

A phased approach to chemical, physical and biological analysis is proposed, which is generally applicable. The approach promises to be cost and information effective as a component of an overall environmental sampling and analysis plan. The advantages over alternative, direct approaches would seem to be the possiblity of comprehensive survey of *all* process streams within the limits of finite resources for process and control technology development.

Table 3. Comparison of NAA and SSMA analysis of coal sample

COAL
µg/gram of Sample

	Neutron Activation*	Spark Source*		Neutron Activation	Spark Source
Li		(<.2)	Se	1	1
Be		(<.2)	Br	10	2
B		50	Rb		20
F		5	Sr		30
Na	2000	3000	Y		3
Mg		800	Zr		4
Al		6000	Nb		1
Si		9000	Mo		3
P		5	Ru		.5
S		900	Pd		.3
Cl	1100	1500	Ag		.3
K	2000	5000	Sb	0.5	.3
Ca	4000	4000	Cs	0.8	1
Sc	3	10	Ba		30
Ti		500	Eu	.2	-
V		20	La	4	2
Cr	50	30	Ce		3
Mn	160	160	Pr		1
Fe	11000	6000	Nd		3
Co	4	5	Gd		1
Ni		25	Pb		1
Cu		10	Th		<1
Zn	60	4	U		<1
Ga		5	Sm	0.8	-
Ge		8	Hg	0.05	-
As	2	20	Cd	4	-

*Mean values, carrying a variability of +2, -1/2 of mean value

EVALUATION OF PARTICULATE CHARACTERIZATION TECHNIQUES*

H. Mahar, Ph.D.
N. Zimmerman, Ph.D.†

Abstract

The Environmental Protection Agency's measurement program for environmental assessment is addressing the need for a rapid, effective, and inexpensive means for evaluating the potential environmental hazards associated with industrial particulate emissions. Chemical analyses and cellular biological assays were performed on size-classified particulate material collected at nine industrial sites. The exercise was formulated to determine whether the chemical analyses or the bioassays, alone or in combination, were sufficient to assess the hazards associated with particulate emissions.

This program has identified the need for size-classified particulate matter to be utilized in the various chemical or biological tests. Elemental analysis and partial organic characterization of the particulate samples have been performed. A cellular bioassay, utilizing rabbit alveolar macrophages (RAM), has been used to provide a rank ordering of particulate samples in terms of their observed cytotoxic activity. A screening technique utilizing several bacterial indicator strains is being used to evaluate the mutagenic potential of the particulate samples. Attempts to correlate observed biological activity with chemical analyses are ongoing.

Several proposed screening methods which may be used to characterize the potential hazards associated with particulate material released from various sources are currently being field tested. Both biological activity and chemical composition of the various samples are being determined. Chemical analysis, when used alone, cannot provide sufficient data for complete evaluation of pollutant emissions due to the effects of synergism, antagonism, and differing degrees of biological availability. The presence or absence of given toxic components does not preclude nor indicate the relationship of the effluent to a suspected toxic effect. Bioassay techniques, on the other hand, can be used effectively to assess potential toxic effects, including interaction effects.

Whereas cellular bioassay takes into account the biological activity of the sample, including synergistic and antagonistic effects, it in no way pinpoints the specific compounds responsible. The most cost-effective screening method would appear to involve the use of cellular bioassay to determine which effluent samples are biologically active, together with the use of chemical fractionation and analysis to ascertain which agents are responsible for the observed activity.

Size-classified particulate material collected at nine industrial sites has been subjected to chemical analyses and biological assays to determine whether the procedures, alone or in combination, provide a rapid, effective, and inexpensive means to evaluate potential hazards associated with particulate emissions. The exercise was formulated to provide actual field testing data to verify the measurement program for environmental assessment being initiated by the Process Measurements Branch, Industrial Environmental Research Laboratory (IERL/RTP), Environmental Protection Agency. The measurement program has been designed to provide a cost-effective means to determine the magnitude of the potential environmental problems associated with emerging energy technologies during the various development stages of that technology (refs. 1,2). The measurement program provides for multiphase testing and characterization, with increased effort directed towards those process or effluent streams identified as potential hazards.

Inorganic elemental analysis and partial organic characterization, with emphasis on polycyclic hydrocarbons of known carcinogenic potential, have been instituted. The rabbit alveolar macrophage cytotoxicity bioassay and mutagenicity screening tests using several bacterial strains *(Salmonella typhimurium)* are utilized to predict the acute toxicity and mutagenic behavior of the particulate matter.

This research program will evaluate these biological and chemical tests, performed alone and in combination, for their ability to assess the potential hazards associated with particulate emissions. An ancillary objective will be to consider the need for and performance of the sequential cyclone sampling train used to collect the particulate sample. At this time, however, the exercise is not complete and only preliminary conclusions can be drawn.

---

*This work was carried out under Contract No. 68-02-1858 with the Environmental Protection Agency.

†The authors are members of the technical staff, Environmental Planning and Engineering Department, MITRE Corp., McLean, Virginia.

SAMPLE COLLECTION

A series cyclone sampling train was developed to provide a capability to collect large quantities of size-classified particulate matter from a variety of industrial sources so that chemical and biological characterizations of the sample could be achieved. The cyclone train design called for collection of samples according to particle aerodynamic diameter in ranges of >10μ, 3-10μ, 1-3μ, and <1μ (by filter). The sampling train was intended to provide representative material from the different industrial sources.

TRW Systems Group* fabricated the sampling train according to drawings provided by Southern Research Institute† (SRI). Since particulate samples were to be collected for cytotoxicity testing, construction materials were selected for their nontoxic qualities. Assessment of toxicity was based upon information generated by TRW on the NASA-sponsored Viking Biology Lander Instrument Program. The field sampling configuration of the series cyclone train is presented in figure 1. The sampling train, as prepared by TRW Systems Group, should not be considered optimal since the intent was to provide a fail-safe sampling system capable of collecting a variety of particulate samples under a variety of operating conditions. In its report, TRW Systems Group urges that the train be redesigned and recalibrated to minimize weight, to reduce the number of components, and to identify more precisely the minimum critical flow that gives acceptable size classifications (ref. 3).

Industrial sites sampled were selected to provide particulate material possessing a variety of physical and chemical characteristics, as well as an anticipated range of cellular toxicity. In order to evaluate the cyclone train, a wide range of sampling conditions under which the train would operate was chosen. Table 1 provides the sampling logistics at nine industrial sites. A tenth site was sampled, but due to unexpected changes in source emission levels, the sample mass collected was too small to permit further analysis. Note that the actual sampling locations at the industrial sites were not consistent with respect to control devices. The particulate material collected should not be construed to represent the actual emissions of that particular site. All sampling, handling, shipment, and storage procedures were intended to provide minimal contamination in subsequent chemical and biological characterizations. An intensive effort was expended during field operations to ensure sample integrity.

CHEMICAL ANALYSIS

Three types of chemical analyses have been performed on the 3-10μ and 1-3μ sized particulate samples. Assays were performed for 75 different elements using spark source mass spectrometry (SSMS). The SSMS technique provided a lower detection limit of 0.1 parts per million by weight (ppmw) for each element. No repetitive analyses of individual particulate samples were performed. Polycyclic organic constituents of the particulate samples were determined using gas chromatographic mass spectrometry (GC-MS) and high resolution mass spectrometry (HRMS). The identification of the polycyclic hydrocarbons focused on those of known carcinogenic potential or of structurally similar compounds. Using GC-MS, the detection limit for individual hydrocarbon species was slightly less than 10 ng. No repetitive analyses of individual particulate samples were performed.

BIOLOGICAL ASSAYS

In this study, two *in vitro* biological assays have been utilized to determine the acute toxicity and the mutagenic potential of the 3-10μ, 1-3μ, and <1μ particulate samples from the various industrial sources. The mutagenic bioassay utilizes several bacterial indicator strains (histidine deficient *Salmonella typhimurium*: TA-1535, TA-1537, and TA-1538), with reversion to prototrophy indicative of mutation (ref. 4,5). Bacterial exposure to the particulate samples, using dimethylsulfoxide as the solvent vehicle, occurs on plates by the agar overlay method. All tests are run with and without a mouse liver activation system.

The rabbit alveolar macrophage (RAM) has been used to determine the potential acute cytotoxicity of size-fractionated particulate matter collected from a variety of industrial sources. The alveolar macrophage exists as a pulmonary free cell and provides an early line of defense against inhaled foreign bodies. Because of its phagocytic activity, it is particularly useful in the toxicologic evaluation of airborne particulate material.

The RAM testing procedure is a modification of that developed by Waters et al. (refs. 6,7). An initial cytotoxicity screening of a particulate sample at a final concentration of 1,000μg/ml of culture medium was performed in triplicate. The particulate sample was incubated for 20 hours in the culture medium to allow for dissolution of any soluble component(s) of the particulate matter. Macrophage cells were then added to achieve a final concentration of approximately 5×10^5 cells/ml. The cultures were then incubated for 20 hours (@ 37° C in a humidified 5 percent CO_2 atmosphere). Cell number was estimated by hemocytometer count and cell viability was estimated by light microscopy on the basis of trypan blue dye exclusion.

---

*One Space Park, Redondo Beach, California 90278.

†200 Ninth Avenue, South Birmingham, Alabama 35205.

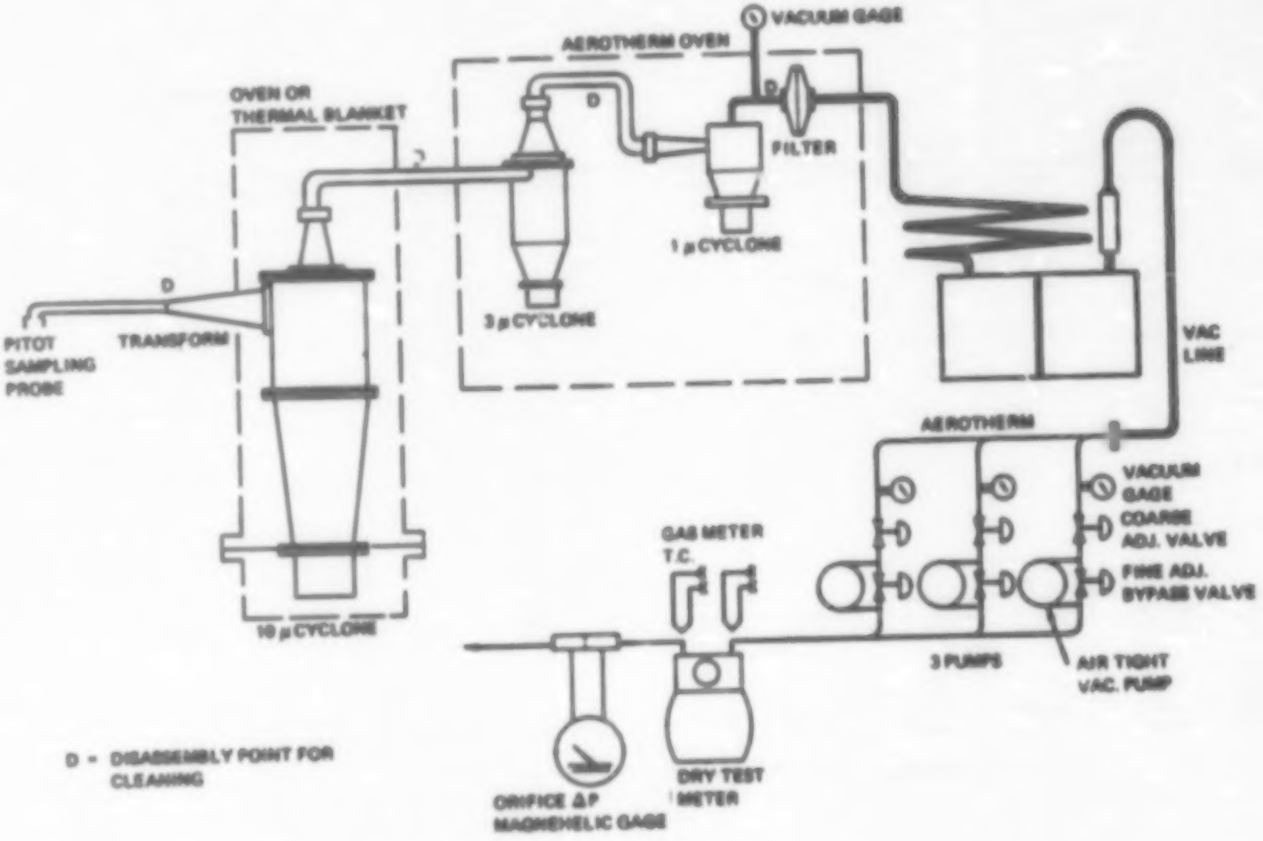

VACUUM GAGE
AEROTHERM OVEN
OVEN OR THERMAL BLANKET
D
FILTER
1 μ CYCLONE
3 μ CYCLONE
PITOT SAMPLING PROBE
TRANSFORM
VAC LINE
AEROTHERM
VACUUM GAGE
COARSE ADJ. VALVE
FINE ADJ. BYPASS VALVE
GAS METER T.C.
3 PUMPS
AIR TIGHT VAC. PUMP
10 μ CYCLONE
D - DISASSEMBLY POINT FOR CLEANING
DRY TEST METER
ORIFICE ΔP MAGNEHELIC GAGE

Figure 1. Series cyclone train, field sampling configuration.

Table 1. Logistics of sample collection

SOURCE	OPEN HEARTH FURNACE	COKE OVEN HEATER	BASIC OXYGEN FURNACE	IRON SINTERING	OIL FIRED POWER PLANT	CERAMICS PLANT (ROTATING KILN)	COPPER SMELTER	ALUMINUM REFINERY	WASTE WATER TREATMENT PLANT, SLUDGE INCINERATOR
SAMPLING LOCATION	ELECTROSTATIC PRECIPITATOR (4 DUCT DIAMETERS DOWNSTREAM FROM ESP, 4 DUCT DIAMETERS UPSTREAM OF STACK)	BASE OF STACK	DOWNSTREAM OF ESP. DOWNSTREAM OF INDUCTION FAN. UPSTREAM OF STACK	INLET TO BAG HOUSE	WET SCRUBBER INLET	BETWEEN PRIMARY AND SECONDARY CYCLONE SYSTEM	OUTLET OF ROASTER DEHUMIDIFIER, INLET TO BAG HOUSE	INLET TO BAG HOUSE	DUCT BETWEEN FURNACE AND WATER QUENCH
T°_{STACK}*	350° - 625°	600°	150° - 225°	400°	170°	510°	250°	230°	1100°
$T^{\circ}_{CYCLONE}$* (10μ)	350°	300°	270°	350°	195°	400°	275°	300°	410°
T°_{OVEN}*	350° - 400°	300° - 400°	270°	300°	250°	400°	300°	300°	300°
FLOW RATE THROUGH SAMPLING TRAIN	4.0 SCFM	3.5 SCFM	4.6 SCFM	5 SCFM	4.5 SCFM	3.0 SCFM	4.7 SCFM	5 SCFM	4.7 SCFM
TOTAL SAMPLING TIME	5 HOURS (CONTINUOUS)	5 HOURS (CONTINUOUS)	5 HOURS (CONTINUOUS)	2 HOURS (INTERMITTENT)	2 HOURS (CONTINUOUS)	1.25 HOURS (INTERMITTENT)	1 HOUR (CONTINUOUS)	2 HOURS (INTERMITTENT)	5 HOURS (CONTINUOUS)

* DEGREES FAHRENHEIT

Samples found in the initial screening to produce net cell death of greater than 15 percent, as compared with controls, were retested in a preliminary concentration-response test using particulate concentrations of 1,000μg/ml, 300μg/ml, and 100μg/ml of culture medium. The pH values of the cultures were monitored throughout, and if shifts below 6.8 or above 7.6 occurred, the sample was tested under both unadjusted and adjusted conditions.

In addition, an attempt was made to ascertain whether the toxicity of a given particulate sample was due to the particles themselves and/or soluble component(s) released into the medium. The particulate matter was incubated in the culture medium for 20 hours and then removed from the medium via centrifugation. The supernatant and centrifuged particles (resuspended in fresh medium) were then tested for cytotoxicity. Figure 2 indicates the testing sequence used in this study.

RESULTS

Analytical results presented here have been chosen for illustrative purposes.* Particulate samples collected in the largest cyclone (>10μ) were not analyzed because it was felt they represented a minor air pollution hazard since they would, in all probability, settle out of the atmosphere in a short period of time. Those particulate samples collected on filters (<1μ) were subjected only to partial organic characterization by GC-MS and to acute cytotoxicity screening by the RAM procedure.

Selected results of spark source mass spectrometry analyses are provided in table 2. For brevity, the concentrations of only 20 of the 75 elements assayed are included. Selection of those 20 elements was based upon Threshold Limit Values (TLV's), concentration, and inherent toxicities. The partial organic characterization of the samples, accomplished by gas chromatographic mass spectrometry, is provided in table 3. Only those organic species present in detectable amounts are listed. Note that three particulate samples were not analyzed (i.e., coke oven heater, 3-10μ sample; oil-fired power plant, 1-3μ and 3-10μ samples). Regarding table 3, it is noted that if collection cyclones were operating at temperatures above 350° F, much of the organic fraction would have been lost as vapor (see table 1).

Selected results of the rabbit alveolar macrophage (RAM) cytotoxicity tests are reported in figures 3 and 4 to indicate the utility of the testing procedure. The graphic displays provide mean values ± one standard deviation. Figure 3 indicates the relative ranking of cytotoxic particulate samples collected from nine industrial sources. Cytotoxicity is reported as percent viability (percent of viable cells remaining after exposure period) at a particulate concentration in the test medium of 1,000μg/ml. The data represent an average observed cytotoxicity from both the initial screening test and the preliminary concentration-response test (@ 1,000μg/ml) including pH adjusted and unadjusted conditions (i.e., there were six determinations for each sample).

Figure 4 provides preliminary concentration-response relationships between different fractions of particulate samples collected from a sludge incinerator. The log of the particle concentration in the test medium is plotted against the viability of the RAM cells, reported as percent of controls (i.e., percent survival) for the particulate plus supernatant (P+S) fraction, the particulate (P) fraction, and the supernatant (S) fraction. In figure 4, the least-squares regression lines for the data are provided along with mean values (± one standard deviation) of the observed viability, reported as percent of control. Note that the 1-3μ sample appears more cytotoxic than the 3-10μ sample.

The bioassay screening procedure to determine the mutagenic potential of the various particulate samples has not been completed. No conclusions can be drawn at this time.

SUMMARY AND CONCLUSIONS

The utility of several testing methods to assess the potential hazards associated with industrial particulate emissions has been established. A rigorous statistical evaluation is underway to identify any relationships that exist between observed biological activity and resultant chemical characterizations. Several preliminary conclusions can be drawn from the completed work:

a. The cyclone train has proven itself a useful tool for the gathering of size-classified particulate material present in a variety of industrial effluents. It has also been shown that the samples collected in 1-5 hours of sampling train operation are of sufficient mass to be utilized for biological and chemical analyses. Furthermore, the need for size-classified particulate material has been established, since the bioassays and chemical analysis have indicated that particulate fractions from the same industrial source do not necessarily possess similar characteristics.

b. Initial studies indicate the potential value of the RAM cyctotoxicity test as a preliminary screen to assess the toxicity of particulate material. The procedure can be used to provide a rank

---

*Complete tabulations are available from the authors.

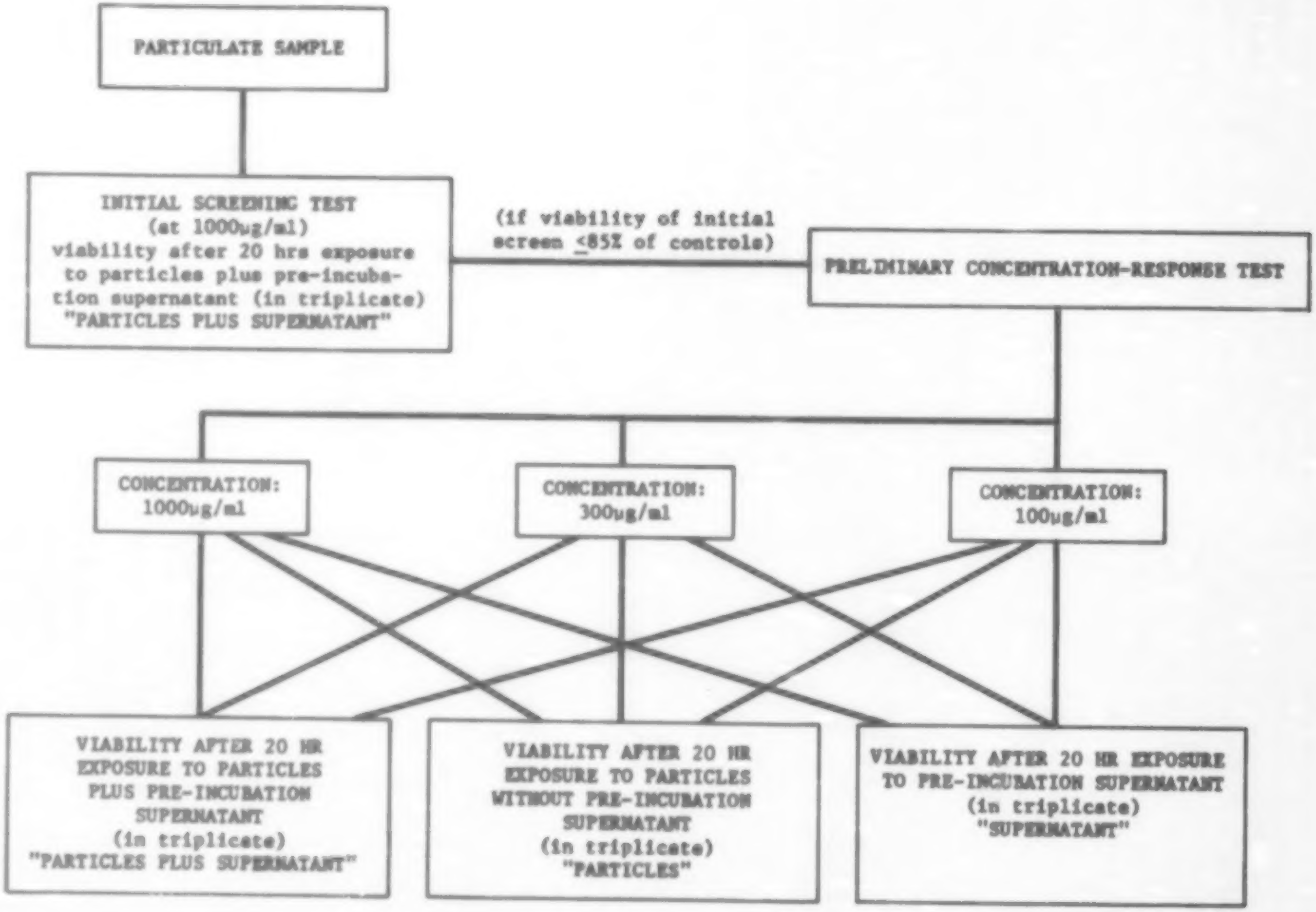

PARTICULATE SAMPLE
INITIAL SCREENING TEST (at 1000µg/ml) viability after 20 hrs exposure to particles plus pre-incubation supernatant (in triplicate) "PARTICLES PLUS SUPERNATANT"
(if viability of initial screen ≤85% of controls)
PRELIMINARY CONCENTRATION-RESPONSE TEST
CONCENTRATION: 1000µg/ml
CONCENTRATION: 300µg/ml
CONCENTRATION: 100µg/ml
VIABILITY AFTER 20 HR EXPOSURE TO PARTICLES PLUS PRE-INCUBATION SUPERNATANT (in triplicate) "PARTICLES PLUS SUPERNATANT"
VIABILITY AFTER 20 HR EXPOSURE TO PARTICLES WITHOUT PRE-INCUBATION SUPERNATANT (in triplicate) "PARTICLES"
VIABILITY AFTER 20 HR EXPOSURE TO PRE-INCUBATION SUPERNATANT (in triplicate) "SUPERNATANT"

Figure 2. Rabbit alveolar macrophage cytotoxicity screening test procedure

Table 2. Partial elemental analysis of particulate samples as determined by spark source mass spectrometry

SOURCE / SIZE / ELEMENT	OPEN HEARTH FURNACE		COKE OVEN HEATER		BASIC OXYGEN FURNACE		IRON SINTERING		OIL FIRED POWER PLANT		CERAMICS PLANT		COPPER SMELTER		ALUMINUM REFINERY		SLUDGE INCINERATOR	
	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ
Bi	21	11	60		2.9	3	100	5.7	1.1		140	79	2%	2%	270	59	1500	1900
Pb	1900	900	940		210	170	5000	2100	450		60	33	35%	6%	300	78	1200	2200
Tl	3.3	0.53	7.5		0.97	0.78	35	11	0.78		10	5.3	3900	1100	3	0.19	2.5	5.3
Te	0.4	0.15	0.85		0.08	0.15	2	0.58	0.12		2.7	1.3	3600	1300	26	6.3	0.29	0.36
Sb	70	27	3.7		9.7	17	3.5	2.5	7.8		10	5.3	8%	3%	130	66	25	30
Sn	610	360	56		40	140	6.1	4.4	14		36	2.9	6%	4000	100	33	1%	3000
Cd	66	5.4	9.6		12	9.7	22	14	0.97		13	6.6	5000	1400	16	1.8	630	790
Ag	65	41	6.2		63	460	35	6.3	4.4		0.57	0.64	1100	2200	2	1.1	600	300
Mo	79	35	17		30	30	17	11	816		23	12	500	2500	69	51	110	33
Se	7.3	2.7	9.8		0.6	0.53	310	89	63		42	20	3000	3600	22	14	73	52
As	480	390	3.9		52	67	120	15	9.3		890	110	21%	6%	4100	700	100	63
Zn	2%	2%	1100		4400	3000	1100	760	900		300	220	1.7%	0.7%	160	56	3000	3000
Cu	2900	3600	170		800	1100	2200	1000	300		210	93	5%	20%	2000	4600	3%	3%
Ni	470	490	31		46	93	64	26	5.2		88	36	1900	760	2000	3000	4500	3000
Co	111	120	2.6		57	130	19	86	220		1.4	18	180	460	43	27	850	1000
Mn	4400	5000	250		3000	1%	314	640	220		1600	1000	310	600	20	6.3	850	1000
Cr	860	880	94		170	220	52	76	1000		150	120	190	79	90	56	4000	2300
V	210	290	38		23	40	33	48	2%		540	210	49	98	5000	1500	94	55
Ti	15	13	8		9.6	0.44	170	290	210		5000	5000	560	1100	130	160	5000	3800
Be	0.36	0.26	0.25		0.13	0.26	0.39	0.57	8.1		2.3	1.2	5.9	0.59	2.9	1.8	2.6	16

*VALUES IN PPM WEIGHT, EXCEPT AS NOTED

Table 3. Carcinogenic and structurally similar polycyclic organic constituents in particulate samples as determined by gas chromatographic mass spectrometry[a]

SOURCE	OPEN HEARTH FURNACE		COKE OVEN HEATER		BASIC OXYGEN FURNACE		IRON SINTERING		OIL FIRED POWER PLANT		CERAMICS PLANT		COPPER SMELTER		ALUMINUM REFINERY		SLUDGE INCINERATOR	
PARTICLE SIZE	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ	1-3μ	3-10μ
IDENTIFIED COMPONENT																		
Anthracene/Phenanthrene	2.7	0.4	3.9	b	24.8	6.9	289.5		b	b	22		0.5		24.7	172.6		
Methyl anthracenes							27.4								9	51.3		
Fluoranthene	1.3	0.2			7.4	1.4	31.2				6.2				34.1	137.2		
Pyrene	0.4				2.9	1	16.1				4.1				42.9	155.8		
Methyl Pyrene/Fluoranthene							18.0				3.9				32.5			
Chrysene/Benz(a)anthracene	0.4						1.9								93.6	287.3		
Methyl chrysenes															25	79.7		
Benzo fluoranthenes	1.6	0.5			1.6		1.8				5.8				248	786.3		
Benz(a)pyrene	0.9	0.3					4.3				5.8				46.5	405.6		
Benz(e)pyrene	3	2			1.8		9.0				13.8				807.2	1014		
3-Methylcholanthrene															59.5	23.5		
Indeno(1,2,3,-cd)pyrene	1.1						10G				3.6				341.4	269.2		
Benzo(ghi)perylene	0.4						0.5				0.8				426	786.3		
Dibenzo(a,h)anthracene	4.3										4.5				1387	1213.3		
Dibenzo(c,g)carbazole															84.7	77.6		
Dibenz(ai and ah)pyrenes	1.5														352	216.1		
Coronene															87.3	50.2		

[a] reported as parts per million by weight

[b] not analyzed

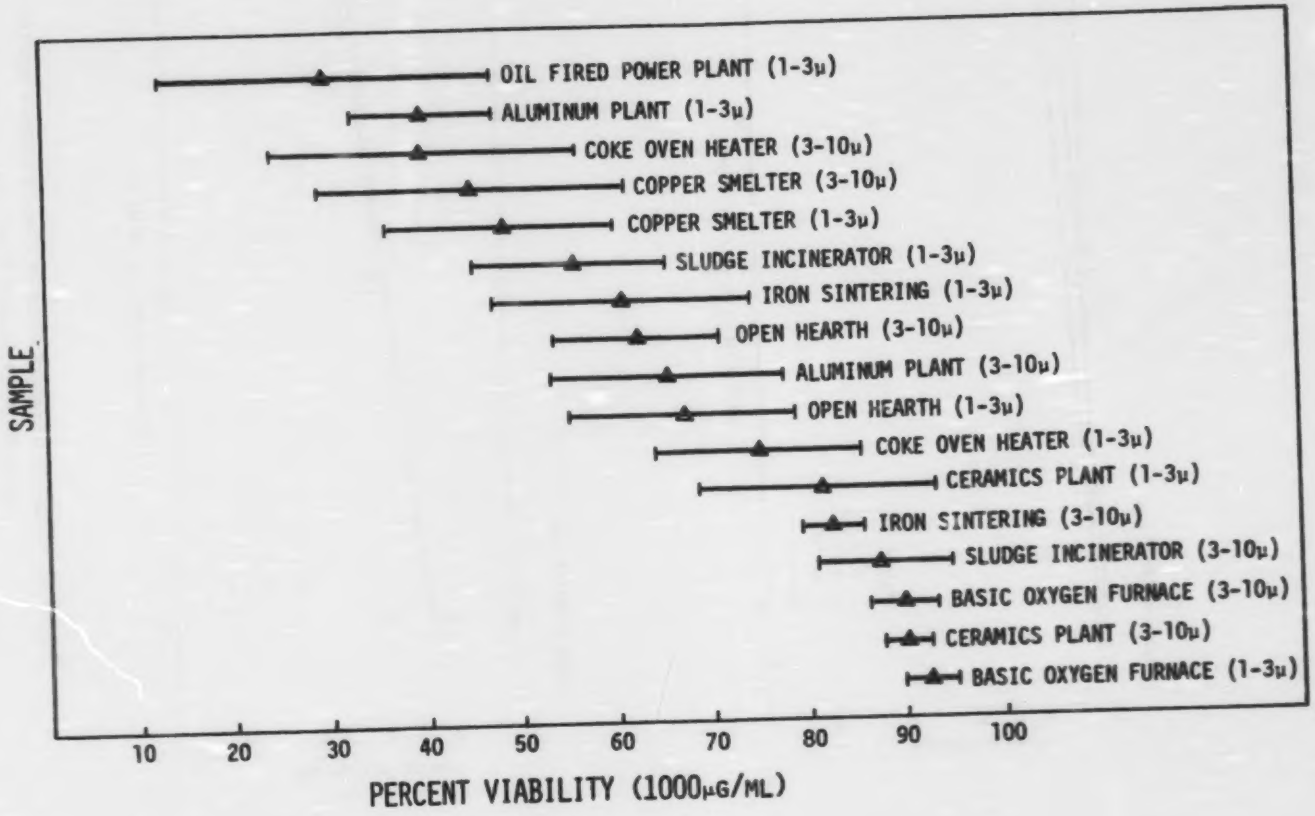


Figure 3. Viability of rabbit alveolar macrophages after 20 hours/particles plus supernatant (data reported as percent viability ± 1 standard deviation; data include screening and preliminary concentration-response trials at the 1,000 μG/ML particle concentration).

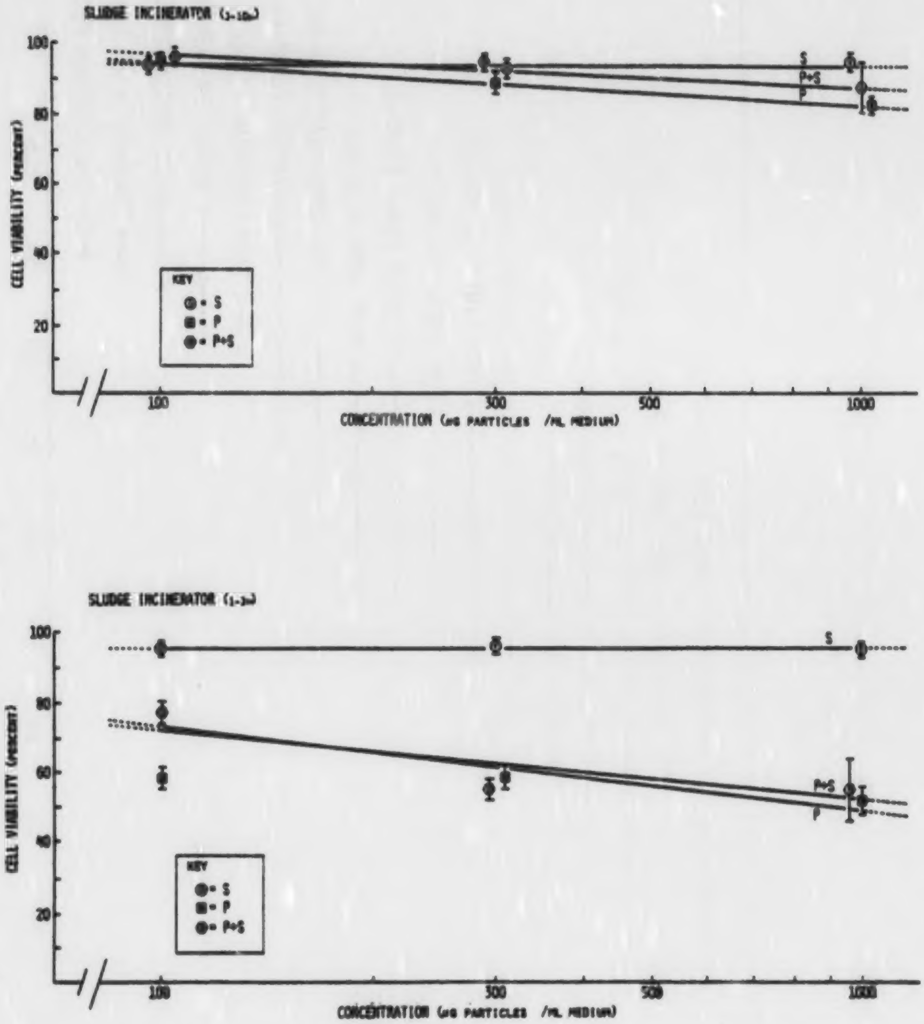


Figure 4. Viability of rabbit alveolar macrophages exposed to various particulate fractions

ordering of samples from industrial sources in terms of their acute cytotoxic behavior. Additional functional and biochemical measurements can be made to enhance the resolution of the bioassay system.

It should be clearly understood that this has been a preliminary report, the purpose of which was to assess selected testing methods of characterizing the potential hazards associated with particulate emissions. Refinement of these methods, including assessment of sensitivity, specificity, and external validity, is of current concern. A comprehensive report on these activities will be available in the first quarter of 1976.

REFERENCES

1. R. M. Statnick and L. D. Johnson, "Measurement Programs for Environmental Assessment," presented at the EPA Symposium, Environmental Aspects of Fuel Conversion Technology, II, Hollywood, Florida, Dec. 15-18, 1975.
2. C. H. Lochmüller, "Analytical Techniques for Sample Characterization," presented at the EPA Symposium, Environmental Aspects of Fuel Conversion Technology, II, Hollywood, Florida, Dec. 15-18, 1975.
3. TRW Systems Group, "Fabrication and Calibration of a Series Cyclone Sampling Train" (Interim Report), April, 1975.
4. F. Gletten, V. Weekes, and D. J. Brusick, "*In Vitro* Activation of Chemical Mutagens. I. Development of an *In Vitro* Mutagenicity Assay Using Liver Enzymes for Activation of Dimethylnitrosamine," *Mutation Res.*, 28:113, 1973.
5. B. W. Ames, W. E. Durston, E. Yamaski, and F. D. Lee, "Carcinogens are Mutagens: A Simple Test System Combining Liver Homogenates for Activation and Bacteria for Detection," *Proc. Nat. Acad. Sci.* USA, 70:2281, 1973.
6. M. D. Waters, D. E. Gardner, C. Aranyi, and D. L. Coffin, "Metal Toxicity for Rabbit Alveolar Macrophages *In Vitro*," *Environ. Res.*, 9:32-47, 1975.
7. M. D. Waters, D. E. Gardner, and D. L. Coffin, "Cytotoxic Effects of Vanadium on Rabbit Alveolar Macrophages *In Vitro*," *Tox. Appl. Pharm.*, 28(2):253-263, 1974.

Session V:

ENVIRONMENTAL PROBLEM DEFINITION, PART B

Robert P. Hangebrauck
Session Chairman

Preceding page blank

WATER REQUIREMENTS FOR AN INTEGRATED SNG PLANT AND MINE OPERATION

D. J. Goldstein and R. F. Probstein*

Abstract

Part of the environmental assessment of large plants to make synthetic natural gas from coal is the determination of the water consumed. This is particularly important in the West where coal is available but water is scarce. The water consumed includes not only water for the conversion process but also water evaporated for cooling and consumed in mining, land reclamation, and solids disposal. Published information varies by more than fourfold. In this paper, details of the procedures for determining water requirements are given. The determination of the cost of not evaporating water for cooling but of using air cooling and condensing is also described. It is shown that water requirements are dependent on process design, mine location, and climate and that generalized assessments which are not site specific and design specific are of limited value. It is also shown that the published water requirements for integrated SNG plants and mine operations in the West may be high and that the actual requirements could, depending on the location, be half the lowest estimate to date.

INTRODUCTION

An important part of the environmental assessment of large plants to make synthetic natural gas from coal is the determination of the quantity of water consumed. This is particularly important in the West where coal is available but water is scarce. As examples of the many studies which have required this information see refs. 1-3. These studies conclude that, by about 1980, water may be the resource which limits the development of coal conversion technology.

For a plant making 250 x 10^6 scf/day of SNG, Davis and Wood of the United States Geological Survey (USGS) have summarized the water requirements to be between 8.8 x 10^6 and 38 x 10^6 gal/day (ref. 4). The lower end of this range of water consumption comes from one of two designs for Lurgi process plants to make SNG from Navajo coal in the Four Corners area near Farmington, N.M. (refs. 5-8). From refs. 5-8 we have prepared table 1, in which it should be noted that the figures for the El Paso plant have been scaled from 288 to 250 million scf/day. It is important to remember that table 1 and all the numerical answers given in this paper are illustrative examples. Even for detailed designs, consumed water estimates between different process designs at the same location cannot be expected to agree to within more than 20% at this stage of development. The water requirements shown in table 1 have been divided into four categories under which detailed discussions will be given in this paper; namely (i) process, (ii) cooling, (iii) mining and reclamation, (iv) evaporation, solids disposal and other uses.

The upper end of the range of water consumption comes from the table in ref. 9 which is also reproduced in refs. 4 and 10. With a change of units, the table of ref. 9 is reproduced in table 2. The plant size used in table 2 (250 x 10^9 Btu/day) is within 6% of the plant size used in table 1 (250 x 10^6 scf/day). Tables 1 and 2 are in disagreement. One important reason for this is the assessment of the water required for cooling.

Hittman Associates in a recent report (ref. 11) find that 55-66 x 10^6 gal/day of water are evaporated for cooling in a coal refinery consuming 1.8 x 10^{12} Btu/day of coal. For a plant consuming 3.5 x 10^{11} Btu/day of coal (as do the SNG plants used as examples in this paper), this comes to 10.7-12.8 x 10^6 gal/day. Assuming that about 75% of the makeup water is evaporated and 25% is blown down, the makeup rates would then be approximately 14-17 x 10^6 gal/day. These values are roughly in agreement with the figures of table 2 for a cooling water makeup rate of 3% of the circulating water, which in turn is consistent with a 25% blowdown rate if a cooling water range of 25° F is assumed.

In (ref. 12) cooling water makeup requirements of 20-35 x 10^6 gal/day are suggested, based on a waste heat calculation. The plant is taken to be 60% efficient so that 160 x 10^9 Btu/day are lost by evaporating water. This requires about 16.7 x 10^6 gallons/day evaporated, assuming 1,150 Btu is needed to evaporate a pound of water. The makeup requirements refer to situations where approximately 3% to 5% of the circulating water is evaporated. Here again, we have a number in approximate agreement with table 2 and in disagreement with table 1.

---

*The authors are partners in Water Purification Associates, 238 Main St., Cambridge, Mass. 02142. R. F. Probstein is also a Professor of Mechanical Engineering at the Massachusetts Institute of Technology.

Preceding page blank

Table 1. Approximate water requirements to make 250 x 10^6 scf/day of SNG by the Lurgi process in New Mexico (refs. 5-8)

Quantities in 10^6 gal/day:

	El Paso			Wesco		
	Input	Output	Net Consumption	Input	Output	Net Consumption
Process, including fuel gas generation	5.3	4.4	0.9	5.7	4.9	0.8
Cooling	4.1	0.4	3.7	3.2	0.7	2.5
Mining, reclamation			1.9			1.9
Evaporation, solids disposal, other uses			2.3			2.1
TOTAL			8.8			7.3

Table 2. Water requirements for 250 x 10^9 Btu/day SNG plant (ref. 9)

Quantities in 10^6 gal/day:

	Bituminous & Subbituminous			Lignite		
Water Cooled						
Cooling makeup (% circulating water)	3	5	7	3	5	7
Process water	2.5	2.5	2.5	2.5	2.5	2.5
Boiler makeup	0.6	0.6	0.6	0.5	0.5	0.5
Cooling makeup	17.4	29.0	40.7	14.5	24.2	33.9
TOTAL	20.5	32.1	43.8	17.5	27.2	36.9
Partially Air Cooled						
Process water + boiler makeup (from above)	3.1	3.1	3.1	3.0	3.0	3.0
Cooling makeup (by subtraction from total)	7.1	13.0	18.8	5.8	10.6	15.5
TOTAL (ref. 9)	10.2	16.1	21.9	8.8	13.6	18.5

So far we have been discussing cooling water. Water consumed in (a) mining and reclamation and (b) evaporation, solids disposal, and other uses is stated to be another large need. For example, in table 1 these categories are seen to represent about 50% of the total water requirement for both designs. However, they are sometimes not included in assessments of water consumption and when included are often not detailed or explained. It is one of the theses of this paper that the water requirements for these categories are very much site dependent. Moreover, the published requirements cited for them may be high and that in fact the actual water need may be much more modest.

Water for the process is the smallest quantity but is notable for the very high quality influent need (which is boiler feed water) and very dirty effluent process condensate (ref. 13).

The present paper is a progress report of our ongoing study and gives the detailed procedures necessary for determining the quantities of water consumed. From these details it will become apparent why such widely differing quantities have been recorded and, for specific processes at specific locations, it will be possible from the procedures given to more precisely define the water quantities required for the process, for cooling, for mining, for disposal, and for other uses.

PROCESS WATER

Figure 1 shows a simplified block diagram of the important sections of an SNG plant employing oxygen, along with the principal process influent and effluent streams. The stream numbers in figure 1 are the same as those in table 3, in which illustrative examples of process influent and effluent water quantities are given together with the references from which they were taken or derived. Each example has been verified by a complete hydrogen balance. We emphasize again that these are specific examples and that repeatability to within 20% is all that can be expected between different process designs. In considering the Lurgi process, note that tables 1 and 3 differ because fuel gas generation is not included in table 3 for any of the processes.

The influent streams are mostly of boiler feed quality. Of the effluent streams, the gasifier off-gas condensate stream 5 may be very dirty. The stream can be as low as 95% water with the rest mostly ammonia, carbon dioxide, phenol, and other organic material. The condensate after the shift converter, stream 6, is dirty but not as dirty as stream 5. Stream 7 depends on the gas purification process. Water made by the methanation reaction, stream 8, is high quality water. The quantity of methanation water is dependent on the fraction of the product methane made in the gasifier as is shown in figure 2 which shows the four processes listed in table 3 along with several other processes.

COOLING WATER USES

As was shown in the Introduction, the published literature contains a fourfold range in the quantity of water required for cooling. In table 4 is given a typical set of thermal data for an SNG plant. This is not for any particular plant but is given so that numerical examples can be provided for this discussion. The assumption that all of the unrecovered heat ends up evaporating water leads to the upper limit of cooling water requirement. To determine whether this is necessary or desirable, we must investigate the points of cooling individually.

In table 5 is shown a partial summary of the relative uses of circulating cooling water for two Lurgi process plants. When water is limited, it is clear that the choice of where to use wet cooling is a matter of engineering discretion. The major sections of an SNG plant using oxygen are shown in figure 1, and our study of numerous detailed plant designs has shown in which of these sections heat is not recovered and in which sections it is either all or mostly recovered (see table 6). In what follows, we will first discuss each section to determine the quantity and level of heat that must be disposed of. Once this has been set forth, we will then point out the considerations necessary to evaluate whether evaporation of water for cooling is necessary or desirable. The actual choice will usually be specific to a process, a design and a climate.

COOLING POINTS AND LOADS

Gas Purification

The energy consumed and the cooling required in gas purification is dependent on the process used. As an example of a chemical absorption process we have considered the hot potassium carbonate process. In our example, 13 x 10^6 scf/hr of CO_2 are to be absorbed. If the liquid absorbs 3.5 scf/gal with an absorber at 1000 psi, the circulation pumps require 4.5 x 10^4 hp. About half of this power can be supplied from a liquid expansion recovery turbine and about 0.15 x 10^9 Btu/hr in steam is consumed by the pump drive, or about 3.3% of the unrecovered heat in the example of table 4. The major energy consumption is in the stripper. The heating load, which is approximately the cooling load, is about 100,000 Btu/1000 scf CO_2 (approximately 10 scf CO_2/lb steam) (ref. 19).* This load is quite low and

---

*During the conference, ref. 28 was brought to the attention of the authors, from which a figure of 80,000 Btu/1,000 scf CO_2 would appear to be more accurate for the high pressures used.

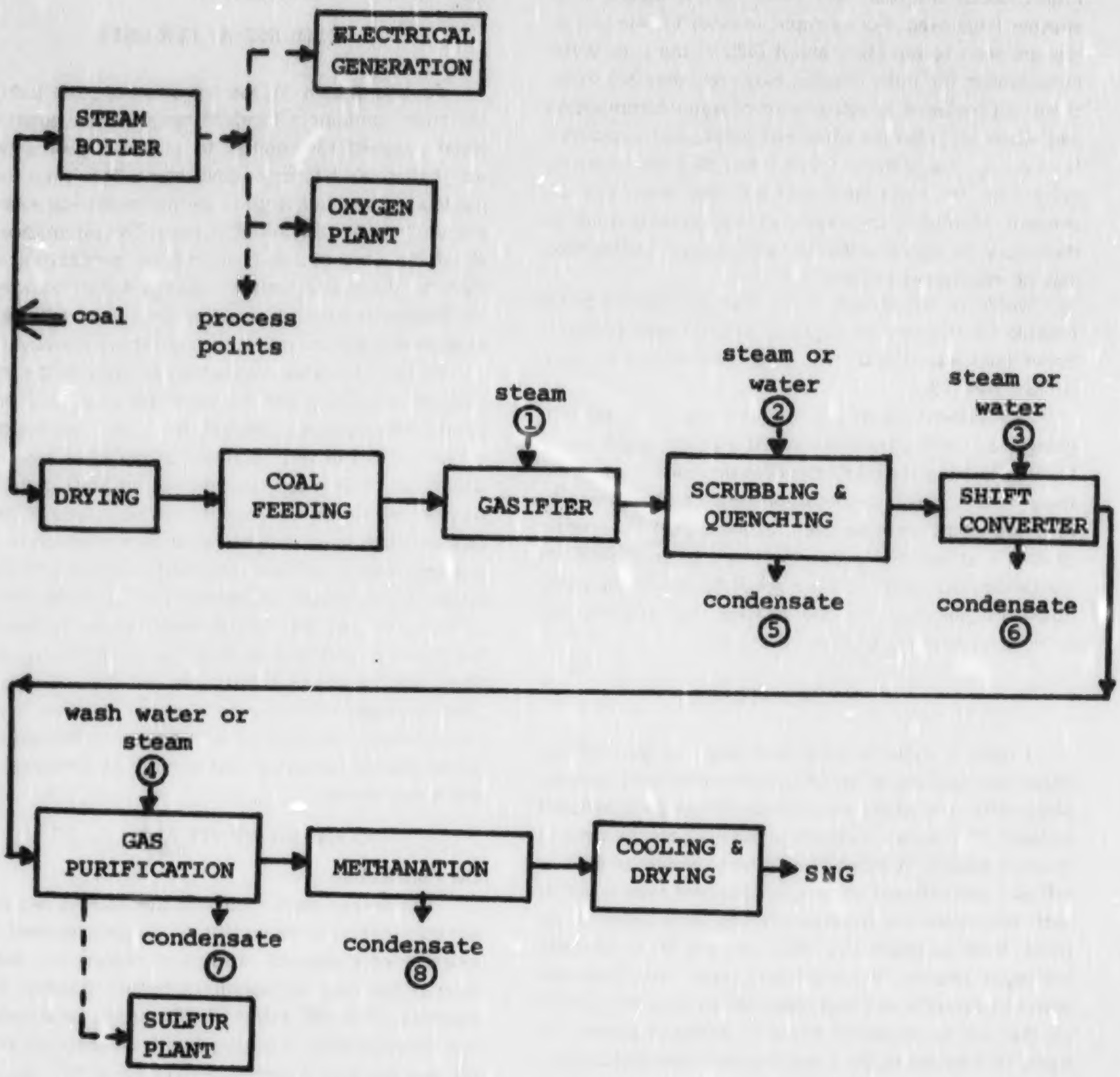

ELECTRICAL GENERATION
STEAM BOILER
OXYGEN PLANT
coal
process points
steam ①
steam or water ②
steam or water ③
DRYING
COAL FEEDING
GASIFIER
SCRUBBING & QUENCHING
SHIFT CONVERTER
condensate ⑤
condensate ⑥
wash water or steam ④
GAS PURIFICATION
METHANATION
COOLING & DRYING
SNG
condensate ⑦
condensate ⑧
SULFUR PLANT

Figure 1. Major sections of an SNG plant

Table 3. Illustrative examples of process water streams for the production of 250 x 10^6 scf/day of SNG

Quantities in 10^6 gal/day:

	Influent Stream					Effluent Stream				
Process	1	2	3	4	Total	5	6	7	8	Total
Lurgi (ref. 5)	4.5	–	–	0.2	4.7	2.9	–	0.2	0.8	3.9
Bigas (ref. 14)	1.2	3.6	0.3	–	5.1	–	2.5	0.4	0.7	3.6
Synthane (refs. 15, 16)	5.0	0.9	–	–	5.9	3.3	1.1	–	0.4	4.8
Hygas/Oxygen (ref. 17)	2.1	3.0	–	–	5.1	–	2.4	0.8	0.2	3.4

applies to a system with a high pressure absorber, such as the one considered; therefore, in our example, 1.3 x 10^9 Btu/hr are consumed as low pressure steam or about 29% of the unrecovered heat in the example of table 4. This heat is removed in the stripping column condenser.

Off-Gas Quenching and Scrubbing

In some plants, the gas leaving the gasifier must be rapidly quenched and scrubbed free of oils and tars. This is done, for example, in the Synthane process. Because the tar is sticky when hot, waste heat recovery is not possible. We find that the quench removes about 1.1 x 10^9 Btu/hr (24% of the unrecovered heat in our example) of which about two-thirds is for condensing steam and one-third is for cooling the gas.

Boiler Steam Generation

Coal, in addition to the quantity consumed in the gasifier, is consumed in the power plant. (In the Synthane process, all the coal is passed through the gasifier and char is burnt in the power plant.) Power is needed to generate electricity, to drive the gas compressors for oxygen production and the big pumps in the gas purification stage. In the simplest case the gas compressors, which are a big consumer of energy, are driven by steam turbines and the steam is condensed as it leaves the turbine. This is an important case for the study of cooling and it is discussed in detail below. However, we must emphasize that this is not the only possibility.

If the coal is of so low a sulfur content that stack gas scrubbing is not required, production of steam by burning coal is probably the best route. If, however, stack gas scrubbing is required, gasification of the coal to produce a low-Btu sulfur-free gas should also be considered. If a low-Btu gas is made, gas turbines will probably also be involved. Even if steam turbines are the only motors used, they are not necessarily condensing turbines.

In our example the extra coal or char burnt for power is 3.2 x 10^9 Btu/hr. In the particular case where this is all burnt to produce steam in a boiler, about 12% of the energy goes up the stack and requires no cooling. This amounts to 0.4 x 10^9 Btu/hr, or 9% of the unrecovered heat in our example.

Oxygen Production

The important details of an oxygen plant are shown in figure 3. Air is compressed to about 90 psia and cooled to about 90° F. In this condition it enters the separation plant which operates with only a small energy and cooling consumption to give oxygen at about 20 psia and about 95° F. The oxygen must then be compressed to gasifier pressure which we have taken to be 1,015 psia. For a discussion on energy and cooling, oxygen production can be treated as a series of compressors.

When a gas is compressed, it heats up and must be cooled before it can be compressed further—that is, coolers are needed between the stages of a compressor. Also, as we are here assuming condensing steam turbine drives for the compressors, condensers are required so that the exhaust steam can be condensed and returned to the boiler. The condensers and the interstage coolers were considered separately for both the air compressor and the oxygen compressor. With the air compressor handling 3.46 x 10^4 lb/min and the oxygen compressor handling 8.06 x 10^3 lb/min, the cooling loads are 0.2 x 10^9 Btu/hr in the air compressor interstage coolers, 0.1 x

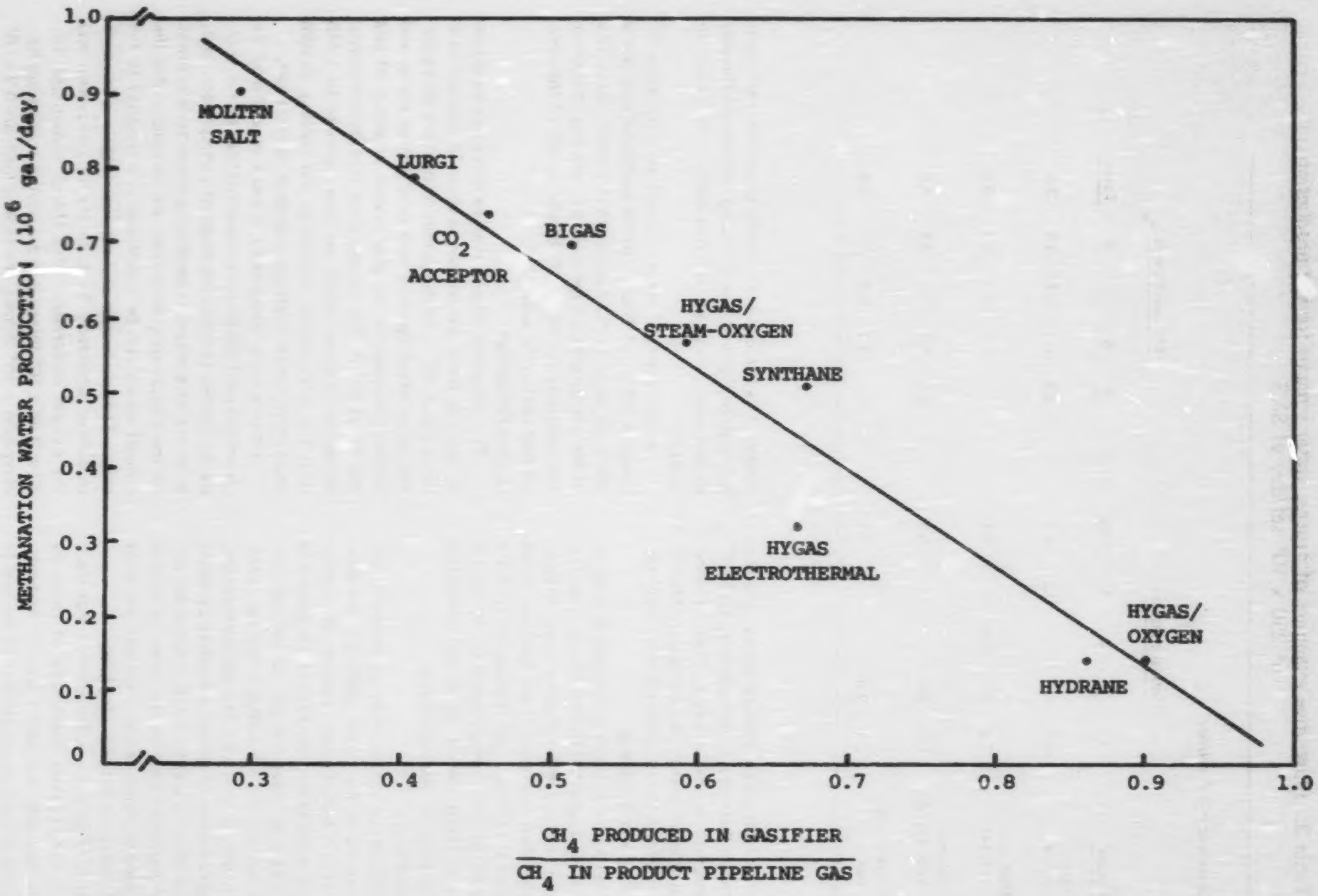


Figure 2. Quantity of methanation water as a function of product methane produced in gasifier for SNG plants producing 250 x 10^6 scf/day.

Table 4. Typical thermal balance of an SNG plant producing 250 x 10^6 scf/day

	Heating Value	
Material	**10^9 Btu/hr**	**% of Feed**
Feed coal	15.0	100
Product gas	(9.8)	(65)
Byproducts	(0.7)	(5)
Unrecovered heat*	Net 4.5	30

*The unrecovered heat if used to evaporate water in a cooling tower, will evaporate about 11.8 x 10^6 gal/day in summer (assuming 1100 Btu/lb water evaporated) or about 10.3 x 10^6 gal/day in winter (assuming 1250 Btu/lb water evaporated). Makeup water quantities will be higher than the evaporated water.

Table 5. Principal uses of cooling water in Lurgi process plants

	Percent of Total Circulated Water	
Section	**(ref. 5)**	**(ref. 18)**
Refrigeration	35	
Gas Liquor Separation	17	
Gas Cooling	11	9
Sulfur Recovery	9	
Phenol Extraction	8	11
Air Separation	8	61
Gas Purification	1	10
TOTAL	90%	91%

Table 6. Disposition of unrecovered heat in SNG plants

Sections Where Heat Is Unrecovered	Sections With Little Unrecovered Heat†
Gas Purification	Gasifier
Scrubbing and Quenching of Gasifier Off-Gas	Methanator
Steam Boilers	Shift Converter
Oxygen Production and Compression	Sulfur Plant
Electrical Generation and Use*	
Coal Drying	
Coal Feeding	
Product Cooling and Drying	

*Unrecovered electrical energy.

†Heat recovery is practiced in most of these sections.

10^9 Btu/hr in the oxygen compressor interstage coolers and 0.6 x 10^9 Btu/hr in the condensers. The total is 0.9 x 10^9 Btu/hr which is 20% of the unrecovered heat in our example.

Electric Power Generation

If steam turbines are used for generating electrical power, then for estimating purposes a heat rate of 10,000 Btu/kwh may be used—that is, an efficiency of about 34%. The amount of electricity used depends very much on the designer. For an example we may consider 18,000 kw to be a middle-to-low requirement. To generate this quantity of electricity, 0.18 x 10^9 Btu/hr are consumed of which about one-third or 0.06 x 10^9 Btu/hr (1.3% of the example's unrecovered heat) is converted to electricity and consumed without cooling and about two-thirds or 0.12 x 10^9 Btu/hr (2.6% of the unrecovered heat) is lost in the turbine condensers.

Coal Drying

The coal fed to many gasifiers must be dry. The energy consumed to dry coal depends on the moisture in the coal. An extreme case is exemplified by a Montana lignite of 30% moisture and 8,700 Btu/lb HHV. To feed 15 x 10^9 Btu/hr to the gasifier, about 0.52 x 10^6 lb/hr of water must be evaporated consuming about 0.5 x 10^9 Btu/hr (11% of the unrecovered heat in our example). Cooling water is not required because if it is used, nearly

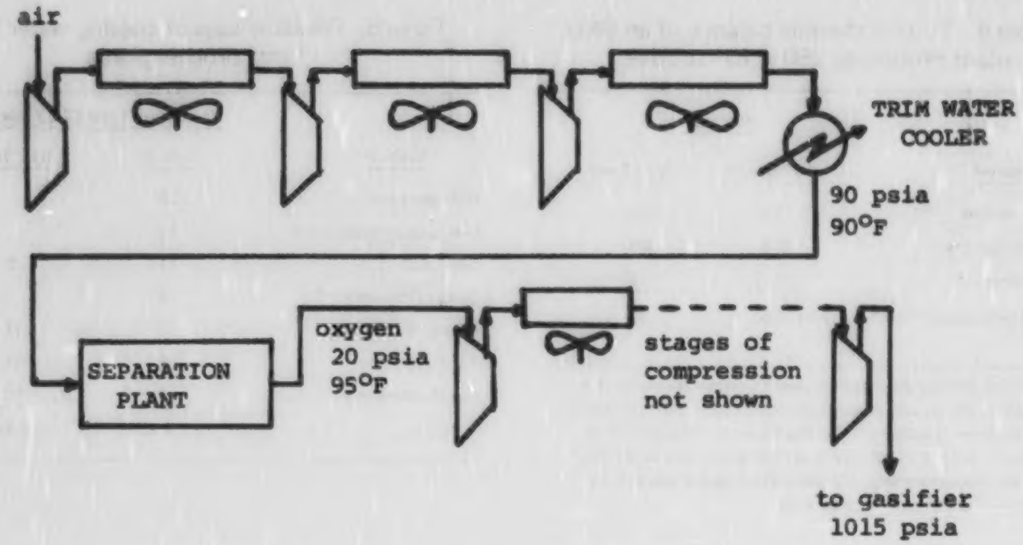


Figure 3. An oxygen plant shown with air coolers.

the same amount of quite clean water would be recovered. We are presently looking into ways of recovering this water using air cooling. For the case considered, were all of the evaporated water recovered, this would amount to 1.3×10^6 gal/day.

Coal Feeding

We have not completed our study of the energy consumed in feeding coal to 1000 psig. If lock hoppers are used, the energy is consumed by the lock hopper gas compressors and the need for cooling water is similar to the discussion on oxygen preparation and electrical generation. If a slurry in toluene is used, the cooling load is that required to condense the toluene in the gasifier off-gas. If a slurry in water is used, it is probable that this water should not be evaporated in the gasifier but should be evaporated before the coal enters the gasifier at 1000 psig—for example, by the hot off-gas from the Bigas gasifier (ref. 20).

Product Cooling and Drying

The SNG product must be cooled and dried. It is necessary to cool to 90° F and not to 140° F because the size of a glycol dehydrator to accept gas saturated at 1000 psig and 90° F must be multiplied by four if it is to accept gas saturated at 1000 psig and 140° F (ref. 41). For purposes of illustration, we have assumed that the gas stream is 250×10^6 scf/day of methane and that it is cooled to 350° F by heat exchange with incoming gas or by waste heat recovery. The total load to cool this gas down to 90° F is about 0.14×10^9 Btu/hr or about 3% of the unrecovered heat in our example.

Summary of Cooling Points and Loads

In table 7, we have summarized the heat dissipation rates required at the cooling points in our illustrative SNG plant. This unrecovered heat load is given in both Btu/hr and as a percent of the total load. The load percentages differ slightly from the percentages cited throughout the text because the total calculated load of 4.7×10^9 Btu/hr is slightly larger than the value of 4.5×10^9 Btu/hr given in the "typical thermal balance" of table 4.

For the particular example given, it is evident from table 7 that there are three principal points of cooling load; gas purification, off-gas scrubbing and quenching, and oxygen production. Another important point to be observed in this regard is that in the example chosen, it is not necessary to supply cooling for 20% of the total "unrecovered heat." Of the remaining 80% of the heat to be dissipated, the three cooling points cited account for about 93% of the cooling which must be supplied.

In the following section, we will attempt to establish the economic and design criteria for determining whether wet, dry, or wet/dry cooling is the desired approach. As previously noted, the choice will usually be site, process, and design specific. We shall only attempt

Table 7. Summary of examples of cooling points and loads.

Point	Load (10^9 Btu/hr)	Load (%)	Cooling Needed
Gas Purification (hot potassium carbonate)			
Regenerator condenser	1.3	28.0	Yes
Pump drive	0.15	3.2	Yes
Off-gas scrubbing & quenching	1.1	23.5	Yes
Boiler steam generation	0.4	8.5	No
Oxygen production			
Air compressor intercoolers	0.2	19.2	Yes
Oxygen compressor intercoolers	0.1		
Turbine condensers	0.6		
Electric power generation			
Turbine condensers	0.12	2.6	Yes
Electricity	0.06	1.3	No
Coal drying (lignite)	0.5	10.7	No
Product cooling & drying	0.14	3.0	Yes
TOTAL	4.67	100	

to outline those calculations and concepts which are important to arriving at a decision.

COOLING METHOD CHOICE

We have investigated the major heat loads shown in table 7 which require cooling, to determine under what conditions dry cooling, wet cooling, or a combination should be used. The formulae and data used in the calculations are given in the appendix. In each case we have determined the cost of water which makes the total annual operating cost equal for wet and dry cooling. The procedure can best be exemplified by detailing the case of gas purification, which is the simplest.

Gas Purification

The condenser in the stripping column of a hot potassium carbonate system must remove 1.3 x 10^9 Btu/hr and can be dry or wet. The vapors were assumed to enter at 230° F and to be cooled to 140° F. Using the information from the appendix, the areas of the condensers were found to be 2.5 x 10^5 ft^2 dry or 1.3 x 10^5 ft^3 wet and the circulation water rate to be 10^5 gpm. The cost estimate is given in table 8. In this example, the choice is between supplying and paying for capital or supplying and paying for water. It should be noted that the cost of water in table 8 and all other tables is for water evaporated and includes the cost of supply, as well as the cost of treating the circulating cooling water and disposing of the blowdown. In the example shown here, dry cooling should probably be used.

Off-Gas Quenching and Scrubbing

The basic system studied for off-gas quenching is shown in figure 4. Circulating quench water is heated from T° F to 270° F in the scrubber and is cooled back to T° F in the cooler, with 1.1 x 10^9 Btu/hr transferred to the cooling medium. The lower the temperature T, the less the energy needed to circulate the water. We have investigated dry cooling with T = 130° F, wet cooling with T = 90° F and with T = 130° F, and dry cooling followed by wet cooling with T = 90° F. In this case, the energy needed to circulate the cooling water more than offsets the larger capital cost of a dry cooler and even with no charge for water, dry cooling is cheaper.

Oxygen Production

By far the most complex optimization of a cooling system is that around the compressors. As part of our ongoing project, we will be doing this optimization at selected sites in the western United States. When, however, one is exploring possibilities with the aim of determining cooling water requirements to an accuracy of

Table 8. Example of a cost estimate for a dry and wet cooled condenser for a hot potassium carbonate gas purification system

		Dry		Wet
Capital Cost			(10^6 $)	
Heat transfer area		4.5		0.66
Cooling tower		–		0.70
	TOTAL (10^6 $)	4.5		1.36
Installed Power			(10^3 hp)	
	TOTAL (10^3 hp)	4.4		4.2
Operating Cost (8000hr/yr)			(10^5 $/yr)	
Capital @ 15%/yr		6.7		2.0
Energy @ 2.24¢/hp-hr		7.8		7.5
Water @ 46¢/1000 gal evaporated		–		5.0
	TOTAL (10^5 $/yr)	14.5		14.5

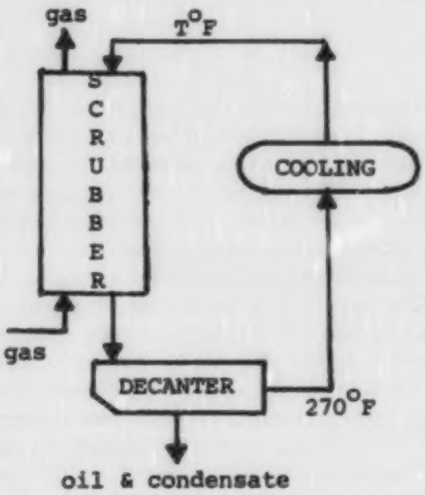


Figure 4. System for off-gas quenching.

about 25%, many of the calculations can be approximated and simplified. We will briefly outline some of the possibilities indicating which have proved to be important. The compressors are to compress 3.46 x 10^4 lb/min of air from 14.7 psia to 90 psia and 8.06 x 10^3 lb/min of oxygen from 20 psia to 1,015 psia. The summer time design conditions are dry interstage cooling to 140° F and wet interstage cooling to 90° F. The maximum exit temperature from a compressor stage is 300° F.

Because the horsepower of a compressor is directly proportional to the absolute temperature of the entering gas, dry interstage cooling will involve more horsepower and a bigger capital investment. This is clearly shown in tables 9 and 10. In winter, when the air and cooling water are colder, the power consumed to compress the gas by a controlled pressure ratio will decrease. When using dry interstage coolers, we have the choice of altering the pitch of the fans to save the fan energy (this is usually done automatically), or of obtaining a lower interstage temperature and saving compressor energy. In this example the compressor energy that will be saved is more than the fan energy, so we assumed that the fans draw full power all year.

When using wet interstage coolers, we will circulate the water at full rate all year to avoid fouling the heat exchangers. However, in the winter, we may operate at one of two extreme conditions or somewhere inbetween. We may run the cooling tower at full capacity. There will be only a small change in the rate of water evaporated, but there will be a large decrease in hot water and cold water temperatures and therefore in the gas temperature entering the compressor stages. This will result in a saving in compressor horsepower.

Table 9. Example of air compressor interstage cooler calculations for dry and wet cooling

	Dry	Wet
Number of Stages	3	3
Summer Design Conditions		
Compressor hp	86,170	81,200
Total dry cooling area (ft^2)	1.62×10^5	–
Total wet cooling area (ft^2)	3.80×10^4	2.43×10^5
Circulated cooling water (gpm)	1.82×10^3	1.52×10^4
Capital Cost	(10^6 $)	
Compressors @ $135/hp	11.63	10.97
Dry cooling area @ $18/$ft^2$	2.92	–
Wet cooling area @ $5.1/$ft^2$	0.19	1.24
Cooling tower @ $7/gpm	0.01	0.11
TOTAL (10^6 $)	14.75	12.32
Auxiliary Power	(10^3 hp)	
Air cooler fans @ 0.015 hp/ft^2	2.43	–
Cooling tower fans @ 0.012 hp/gpm	0.02	0.18
Circulation pumps @ 0.03 hp/gpm	0.05	0.46
TOTAL (10^3 hp)	2.50	0.64
Operating Cost (8000 hr/yr)	(10^6 $/yr)	
Capital cost @ 15%/yr	2.2	1.8
Annual avg. compressor power @ 2.24¢/hp-hr	15.1	14.3
Auxiliary power @ 2.24¢/hp-hr	0.4	0.1
Water @ $8.4/1000 gal evaporated	0.2	1.7
TOTAL (10^6 $/yr)	17.9	17.9

Alternatively we can hold the hot water and cold water temperatures, and so hold the compressor power constant, and bypass the cooling tower—saving water and fan energy. Using, as an example, a climate approximating that of New Mexico, we find that it is best to run the cooling towers at full capacity all year, to save compressor energy and not to save water and cooling tower fan energy.

The results of the interstage cooler sample calculations are summarized in tables 9 and 10. The cost of cooling water is offset by the cost of capital (for the cooling system and for the compressors) plus the cost of energy to drive the compressors. An annual average compressor power has been used in the approximate cost comparisons and because this is so important, the break-even water cost will be dependent on climate. In our examples, wet cooling should probably be used if water is available.

In considering condensers for the steam turbine drives, an additional complication becomes important; the "heat rate," which is the rate of heat consumption per horsepower output, varies with the condenser temperature. We assumed 7,700 Btu/hp-hr below 100° F, 7,800 Btu/hp-hr at 120° F and 8,070 Btu/hp-hr at 140° F. Because the heat rate is not linearly dependent on temperature we have, when using a dry condenser, run the fans all year-round and saved compressor energy; but, when using a wet condenser, we have bypassed the tower in winter and saved water and fan energy. If the tower is bypassed for the condensers and not bypassed for the interstage coolers, two separate cooling tower basins and circulating systems must be installed and maintained.

The approximate cost calculation is shown in table 11. The added compressor energy is due to the change in heat rate and is dependent on the climate; so, therefore,

Table 10. Example of oxygen compressor interstage cooler calculations for dry and wet cooling

	Dry		Wet
Number of Stages	7		5
Summer Design Conditions			
Compressor hp	39,710		38,455
Total cooling area (ft^2)	3.89×10^4		4.99×10^4
Circulated cooling water (gpm)	–		7.26×10^3
Capital Cost		(10^6 $)	
Compressors @ $135/hp	5.36		5.19
Cooling area (see Appendix)	0.70		0.26
Cooling tower @ $7/gpm	–		0.05
TOTAL (10^6 $)	6.06		5.50
Auxiliary Power		hp	
Air cooler fans @ 0.015 hp/ft^2	584		–
Cooling tower fans @ 0.012 hp/gpm	–		87
Circulation pumps @ 0.03 hp/gpm	–		218
TOTAL (hp)	584		305
Operating Cost (8000 hr/yr)		(10^6 $/yr)	
Capital @ 15%/yr	0.91		0.83
Annual avg. compressor power @ 2.24¢/hp-hr	6.99		6.83
Auxiliary power @ 2.24¢/hp-hr	0.10		0.05
Water @ $3.3/1000 gal evaporated	–		0.29
TOTAL (10^6 $/yr)	8.00		8.00

is the breakeven water cost. Wet cooling should probably be used if water is available.

Throughout our calculations so far we have compared wet coolers to dry coolers. In fact, dry intercoolers followed by wet trim coolers are accepted practice. The optimization of these designs is quite complex as may be seen in ref. 21 where it is shown that an optimum pressure drop and heat transfer coefficient exist for the air part of the interstage cooling. In northern climates, a dry condenser can condense at temperatures below 100° F for many months in winter obviating the need for cooling water. Larinoff and Forster (ref. 22) have discussed the various ways of applying dry/wet cooling to turbine condensers (e.g., dual surface dry/wet condensers with a wet cooling tower or a wet condenser with a dry/wet tower in series or parallel arrangement). All of these possibilities represent a potential saving in water at the cost of a higher investment in the cooling system. We will be studying these possibilities.

Product Cooling and Drying

In figure 5 is shown the cost of cooling a high pressure hydrocarbon gas from 350° F to an exit temperature of T° F. The cost is expressed per unit of heat load and, provided the heat transfer coefficients do not change, it does not matter if the heat load includes a condensing load. When cooling SNG, the condensibles are such a small fraction of the stream that figure 5 applies. We have, therefore, chosen to cool the product SNG by dry cooling to 140° F and then by wet cooling to 90° F; 86% of the load is taken by the dry cooler.

Summary of Wet or Dry Cooling Choices and Evaporated Water

Our suggestions for wet or dry cooling are shown in table 12 which is an extension of table 7. Wet cooling has been assumed for the condensers of all drive turbines because the calculation is similar to that for the air and oxygen compressors. The load on wet cooling is about 1.20×10^9 Btu/hr. About 0.95×10^9 Btu/hr is the load

Table 11. Approximate cost comparison for dry and wet compressor turbine condensers

Units in 10^5 \$/yr:

	Air Compressor Drive		Oxygen Compressor Drive	
	Dry	Wet	Dry	Wet
Operating Cost				
Capital @ 15%/yr	3.3	1.0	1.6	0.5
Fans & pump energy @ 2.24¢/hp-hr	4.4	2.5	2.1	1.2
Added compressor energy @ 3¢/10^6 Btu	4.9	–	2.3	–
Water at \$2.[illegible]3/1000 gal evaporated	–	9.1	–	4.3
TOTAL (10^5 \$/yr)	12.6	12.6	6.0	6.0

on turbine condensers and wet cooling of a process stream following dry cooling. If, as we have suggested, this type of cooling load requires a constant cold water temperature all year round with the tower bypassed in winter, the rate of evaporation of water will vary with the climate from site to site. We have made preliminary calculations using the climates of Farmington, New Mexico; Casper, Wyoming, and Bismarck, North Dakota. The annual average rate of heat removal is about 1,100 Btu/lb water evaporated in New Mexico and 1,300 Btu/lb in the more northern locations. This applies to that portion of the cooling load which permits tower bypassing. For estimating purposes then, about 3.1 x 10^6 gal/day of water would be evaporated for cooling in the Four Corners area of New Mexico, while about 2.6 x 10^6 gal/day would be evaporated in the lower Northern Great Plains region of Wyoming. As we have noted, these water requirements are very reasonable estimates and do not necessarily represent minimum values.

WATER CONSUMED FOR OTHER THAN PROCESS AND COOLING

The consumptive water requirements shown in table 1 for (a) mining and reclamation and (b) evaporation, solids disposal, and other uses, together constitute about 50% of the total usage for both Lurgi SNG designs in New Mexico. From these designs (refs. 5-8, 18, 23) we list in table 13 the principal categories of consumed water. The mining and reclamation group is essentially independent of the process, while the other group is somewhat dependent on the process. Both groups, however, depend strongly on the geographical location and we may expect different answers for a New Mexico plant when compared with one in the Great Plains.

In the following sections, we will discuss separately each principal category of water consumption and attempt to provide a general methodology for calculating the amount of water consumed. When water is limited, its use or loss prevention becomes a matter of economic tradeoff. The water quantities we will present will be characterized as reasonable bounds, with no effort made to provide as detailed cost estimating as was done for cooling. Thus, for estimating road dust control requirements, we shall not treat all roads as paved, but neither shall we consider them all unpaved. Similarly, when considering evaporation suppression in ponds, we shall not consider unusual pond depths nor expensive chemical retardent procedures. However, where acceptable procedures exist for conserving water as in sulfur byproduct packaging, these will be noted. On the other hand, where detailed capital cost tradeoffs must be made against water costs, as in boiler tube cleaning of coal-fired boilers, this will also be pointed out. Detailed cost tradeoffs are now being carried out to determine whether water use is necessary or desirable for several special and relatively small categories. These detailed calculations will be reported on at a later date as part of our ongoing program.

MINING AND RECLAMATION WATER REQUIREMENTS

In this section, we will discuss the principal consumptive water requirements for mining and land reclamation associated with an SNG plant producing 250 x 10^6 scf/day. By way of example, we will consider a

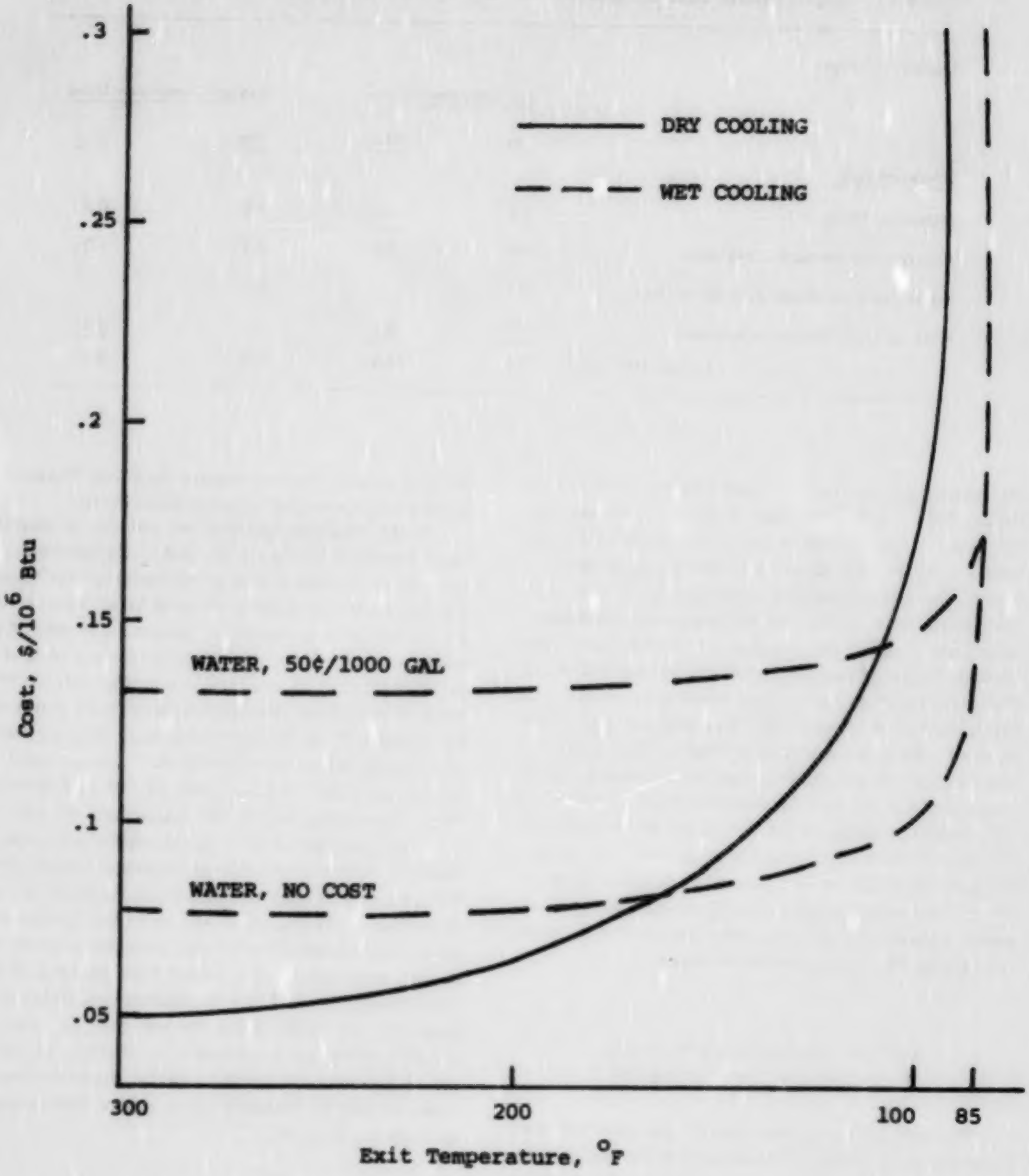


Figure 5. The cost of cooling a high pressure gas stream.

Table 12. Summary of the choice of wet or dry cooling and approximate amount of evaporated water for an SNG plant producing 250 x 10^6 scf/day in New Mexico and Wyoming

Point	Load (10^9 Btu/hr)	Breakeven evaporated water cost ($/$10^3$ gal)	Wet or Dry	Evaporated Water N.M. (10^6 gal/day)	Evaporated Water WYO. (10^6 gal/day)
Gas purification (hot potassium carbonate) Regenerator condenser	1.3	0.46	Dry		
Pump drive	0.15		Wet	0.39	0.33
Off-gas scrubbing & quenching	1.1	zero	Dry		
Boiler steam generation	0.4	no cooling			
Oxygen production					
Air compressor intercoolers	0.2	9.4	Wet	0.53	0.45
Oxygen compressor intercoolers	0.1	3.3	Wet	0.26	0.22
Turbine condensers	0.6	2.6	Wet	1.57	1.33
Electric power generation					
Turbine condensers	0.12		Wet	0.31	0.27
Electricity	0.02	no cooling			
Coal drying (lignite)	0.5	no cooling			
Product cooling & drying	0.14	zero	85% Dry		
			14% Wet	0.05	0.04
TOTALS	4.67			3.11	2.64

Table 13. Principal categories of consumed water in SNG plants for other than process and cooling

Mining and Reclamation	Evaporation, Solids Disposal and Other Uses
Road Dust Control	Pond Evaporation
Coal Handling	Ash Disposal
Coal Washing	Sludge Disposal
Revegetation	Other Uses

plant in which steam is produced in coal-fired boilers. Our emphasis is principally on the difference in water needs between different sites. The absolute values of the requirements given are to some extent a matter of engineering discretion and dependent on a wide variety of conditions. Nevertheless they can be considered to be representative. The locations considered for our examples are the Four Corners area of New Mexico and Campbell County, Wyoming, in the lower Powder River Basin near Gillette, Wyoming. We emphasize that only the principal consumptive requirements are discussed so that, for example, domestic and industrial uses are not considered here, although they will be in the next section, because most of the water is reused.

Road Dust Control

Truck traffic on unpaved haul roads will generally give rise to fugitive dust. The amount of fugitive dust will depend principally on the miles of unpaved road, the traffic density, and the dust raising capacity of the vehicles, which increases with vehicle speed and size. It will, of course, also depend on the soil type and the weather in that more dust will be raised during dry periods or when there is wind.

To a large extent, the length of the haul roads will depend on the area's productivity, as measured by the amount of coal or more exactly, heating value recoverable, per unit area of stripped land. As stripping proceeds, the further out from the gasification plant or the more haul spokes required to obtain the needed coal input, the larger will be the number of miles of haul roads. It follows that the haul road lengths are site dependent. Needless to say, the soil type and weather conditions are also site dependent. In table 14 are shown typical strip-mined coal yields in tons/acre for the Four Corners area of New Mexico and for the Campbell County area in Wyoming, as estimated from the data of refs. 23, 24. Also shown are the corresponding lengths of 45-foot-wide unpaved haul roads, as cited for the proposed Ull-Wesco 9.6 x 10^6 ton/year mining operation (ref. 23), and as estimated for the Arco 10 x 10^6 ton/year Black Thunder Mine (ref. 24). There is no implicit assumption here that the level of truck traffic is the same to yield the same heating value output per year.

Table 14. Typical coal yields and unpaved haul road lengths for a 10 x 10^6 ton/year strip mining operation in Four Corners, New Mexico and Campbell County, Wyoming

	Four Corners, New Mexico	Campbell County, Wyoming
Land yield of 8,500 Btu/lb coal (tons/acre)	37,000	125,000
Total length of 45-ft wide unpaved haul roads (miles)	8	2

One way to essentially eliminate this source of dust is to pave the roads. This involves a cost and in our ongoing program we shall undertake to compare this cost with the costs for alternative methods of holding down road dust. The principal alternative is to wet down the haul roads, with or without the aid of chemical evaporation retardents and soil stabilizing agents. Lacking precise information on road dust suppression, we may assume that the roads can be kept in a wetted condition through an annual deposition rate of water on the roads equal to the net annual evaporation rate. Any rainfall is taken to be an additional safety factor and is not subtracted from the amount of water to be laid down, because how much of it is actually absorbed in the roadway and how much runs off is variable. In table 15, we have shown both the annual precipitation and evaporation rates for the Four Corners area of New Mexico and the Campbell County area of Wyoming. Knowing the evaporation rate, we have evaluated the water requirement for road dust control using the relation

lay down rate = evaporation rate x road length
x road width.

For Four Corners, we find a requirement of 147 gpm and for Campell County, a requirement of 32 gpm. It is of interest to compare these values, respectively, with the estimated annual average of 270 gpm for the Ull-Wesco operation (ref. 27) and the estimated 36 gpm requirement for the Arco Black Thunder Mine (ref. 25).

Table 15. Annual precipitation and evaporation rates for Four Corners, New Mexico and Campbell County, Wyoming (refs. 23, 25, 26)

	Four Corners, New Mexico	Campbell County, Wyoming
Precipitation (inches/year)	8	13
Pond evaporation rate, 90% pan rate (inches/year)	65	56

We would emphasize that the requirements cited can be reduced through the use of chemicals which penetrate the road soil and either stabilize it or retard evaporation. In this regard we would also note that waste blowdown salts might also be put on the road as a means of retarding the evaporation rate. In any event, the example values should be considered maximum ones for the given road areas and that economies in this particular water need can undoubtedly be made.

Coal Handling

In all coal preparation plants dust is generated in the stages of unloading, conveying, crushing, general screening, and storage. The two main categories of dust collection systems employed are wet collectors and dry collectors. For the operations described, dry collectors are most commonly used. Although the amount of dust generated will depend on the coal size required for the process, this obviously can have no direct effect on water needs, so long as dry collectors are employed. In the Wesco Lurgi design, a fabric filter dry dust collection system is planned, so that water will not be required for dust control (ref. 23). Some small amount of water may be needed to wet down storage piles, to prevent fines from becoming airborne during dry periods of high wind, although covered storage areas could minimize this problem. To the extent that the weather depends on the site there can be some variability in this water usage. In any case, the amounts involved would be small enough so that for estimating purposes we need not allocate water for this category of dust control.

A water requirement may be imposed by the fact that different processes require different size coal. For example, a Lurgi gasifier uses relatively large size coal which requires only primary crushing and secondary crushing and screening to yield a 1½" x 0 product. On the other hand, the Synthane and Bigas processes use a 200-mesh pulverized coal. Depending upon the process, some water may be needed for preparing the coal for pulverizing but no general requirements can be stated and, in any case, they would not appear to be large.

Coal Washing

When steam is produced by coal-fired boilers, as in the Wesco Lurgi plant (refs. 8, 23), it may be desirable or necessary to upgrade the run-of-mine coal by reducing the ash and sulfur levels. In the Wesco design, washing pilot plant tests by Utah International Inc., using wet concentrating tables, have led to upgraded properties that are shown in table 16, where they are compared with the properties of the run-of-mine Navajo coal. Also shown for comparison is a representative composite of run-of-mine Wyoming subbituminous coal from beds near Glenrock and Gillette in the lower Powder River Basin. Washing the Navajo coal is seen to decrease the ash by about 52% and the sulfur about 24%, as measured per unit of heating value. Stack gas cleanup for SO_2 removal would still be required to meet the emission standards of 1.2 lb $SO_2/10^6$ Btu.

A wet concentrating table is an easy-to-operate, inexpensive and reliable coal washer. However, it is a relatively large consumer of water. The throughput of water for these devices can be taken to be about 12 gpm per ton per hour of feed coal (ref. 30). Although the makeup water rate is to some extent discretionary, we may use the overall figure for coal preparation plants in New Mexico of about 12%. This value is somewhat lower than the national average of 16.6%, which however includes such water surplus areas as Washington and Alaska, but is higher than in the large water-consuming humid States of Ohio and Pennsylvania where the comparable values are only 8.3% and 10.2%, respectively. It is also higher than for the semiarid mining regions of Montana where it runs at 9.1%. Figures for the other Northern Great Plains regions of interest are not available (ref. 30).

The amount of upgraded coal required for the steam plant is about 3,760 tons/day (157 tph) which may be compared with 21,860 tons/day of run-of-mine coal needed for the gasifier (ref. 23). With about a 30% solids concentration in the tailings from the concentrating tables, we may estimate the sized raw coal fed into the tables at about 175 tph. The consumptive water use is then 175 tph x 12 gpm/tph x 0.12 or about 250 gpm. This may be compared with the average annual value of 450 gpm estimated by Utah International (ref. 27).

From table 16, comparison of the ash and sulfur content of the washed Navajo coal with the run-of-mine Wyoming coal shows clearly that if the same processes were contemplated in the lower Northern Great Plains, the coal would not have to be washed and there would be no associated water requirement.

Revegetation

As part of any reclamation of strip-mined land in arid and semiarid regions there exists a potential requirement for supplemental irrigation water associated with the establishment of soil stabilizing plant cover on mine spoils. A report by the National Academy of Sciences (ref. 26) on the rehabilitation of Western coal lands concludes that areas with greater than 10 inches of mean precipitation annually can be reclaimed without supplemental irrigation, but that with less than 10 inches

Table 16. Properties of Navajo coal before and after washing (ref. 23) and of a composite Wyoming subbituminous coal (ref. 29)

Coal	Ash (wt %)	Sulfur (wt %)	Higher Heating Value (Btu/lb)
Navajo, run-of-mine	26.0	0.96	8,310
Navajo, washed	14.1	0.87	9,870
Wyoming, run-of-mine	6.1	0.62	9,043

supplemental irrigation is required. This conclusion may be somewhat oversimplified in that factors other than precipitation must undoubtedly enter, including the evaporation rate, soil properties, seasonal precipitation periods, land exposure, etc. (ref. 26).

Numerous studies have recently become available on the techniques for reclaiming strip-mined land (refs. 31,32). Among the most recent efforts is an attempt to revegetate mined land in the Four Corners region, where the rainfall is less than 10 inches (see table 16), without supplemental irrigation by using water harvesting techniques. In any case, however, we can conclude that partially reshaped mine spoils can be successfully revegetated in this region with supplemental irrigation of about 10 inches during the first growing season, with no further requirement during subsequent growing seasons (ref. 33).

For the Wesco example of a Lurgi plant in Four Corners, as previously noted, the coal required would be about 9.6 x 10^6 tons/year which, based on the yield shown in table 14, would indicate a mined land area requiring reclamation of about 260 acres annually. The product of the required depth of irrigation water per year and the area of land mined annually leads to a supplemental irrigation requirement for our example of 135 gpm. This requirement is less than the 335 gpm estimated by Utah International (ref. 27) where account was taken of seedlings not taking hold the first season and where higher initial requirements were assumed (ref. 27).

Data on reclamation in Wyoming (refs. 34, 35) indicate that in the Powder River Basin, where the annual precipitation is 12 to 14 inches or somewhat higher, supplemental irrigation is in fact not needed to revegetate mine spoils. Of course, proper reclamation techniques must be followed including returning top soil, slope reduction, grass drilling, timely seeding, fertilizer addition, mulching, etc. (ref. 34). On the basis of the published information, it does appear that water allocation for revegetation is not required in such areas as the Powder River Basin.

Summary of Mining and Reclamation Needs

The importance of site in determining water requirements is perhaps most clearly illustrated from our results for the mining and reclamation examples. In table 17 we have summarized the principal consumptive uses for the mining and reclamation needs associated with an SNG plant producing 250 x 10^6 scf/day in Four Corners, New Mexico and in Campbell County, Wyoming. Two things stand out from these results; the large difference in water needs between the two sites and the fact that even the larger of the two values represents but a small fraction of what had previously been considered to be the total requirements for the plant and mine (see table 1).

CONSUMED WATER IN EVAPORATION, SOLIDS DISPOSAL, OTHER USES

In this section we estimate the amount of water consumed in evaporation, ash quenching, sludge disposal, and other side uses associated with the operation of the gasifier and complex, and with product removal. The consumptions in these categories are somewhat dependent on the specific gasification process employed

Table 17. Summary of principal consumptive water requirements for mining and reclamation examples for an SNG plant producing 250 x 10^6 scf/day

	Four Corners, New Mexico		Campbell County, Wyoming	
	(gpm)	(10^6 gal/day)	(gpm)	(10^6 gal/day)
Road dust control	147	0.21	32	0.05
Coal handling	–	–	–	–
Coal washing	250	0.36	–	–
Revegetation	135	0.20	–	–
TOTAL	532	0.77	32	0.05

and on the plant design, as well as on the site. Whenever possible, we will try to provide a general methodology for determining the amounts of consumed water. Often, however, we will fall back on specific process characteristics associated with proposed Lurgi designs, since most of the published information available for comparison is for these designs.

Pond Evaporation

Any estimate of the amount of water lost through evaporation from settling ponds, reservoirs, or clarifiers at the plant site will depend principally on three factors; (1) the geographical location as it affects precipitation and evaporation rates, (2) the pond areas, and (3) whether evaporation suppressants are used. The first factor cannot be controlled once the plant location has been fixed. To a large extent the pond area is governed by the site, since it affects the quality of the supply feedwater. For plain sedimentation, the dirtier or more turbid the feed, the longer is the settling time and hence the larger is the basin volume, which generally implies a larger basin area. The extent to which use is made of chemical agents, such as lime, to enhance flocculation and speed up the sedimentation process is a matter of economic tradeoff. The use of evaporation suppression techniques is also a matter of economic tradeoff against the price or need for water.

The principal uses for ponding are; (1) settling basins or clarifiers for the supply feed stream, (2) a storage and surge reservoir for the clarified supply, and (3) settling ponds for clarification of water to be recycled, such as water from tailing ponds, etc.

If the volume flow rate (throughput) of water into any pond (basin or reservoir) is known, the water surface area is given by the relation

pond area = throughput x settling time/water depth.

A conservative settling time for a basin to clarify a turbid surface stream, where lime is used as a precipitant, may be taken to be 24 hours. It is also reasonable to assume a 1 week storage in the reservoir to accommodate for any interruption of the supply. Peak usage and surge periods can be accounted for by designing for a throughput which is 50% greater than the mean annual average. For our example of an SNG plant in Four Corners, New Mexico, we estimate the total mean withdrawal from the feed stream to be 3,800 gpm, while for the Campbell County, Wyoming, example, we take 2,600 gpm. Any small changes resulting from a difference in these estimated totals can be accounted for once the plant water requirements are determined in detail. A water depth of 3 ft for the settling basin is characteristic, while 21 ft for the reservoir would be reasonable. These data along with the derived surface areas are shown in table 18.

To estimate the mean loss of water from these holding areas, reference is made to table 15 where it is shown that the annual difference between the precipitation and evaporation is 57 inches in New Mexico and 43 inches in Wyoming. This corresponds to a net evaporation rate of about 0.1 gal/ft^2/day in New Mexico and about three-fourths that value in Wyoming. In table 19 are shown the water loss rates for the surface areas of table 18 based on the net evaporation minus precipitation figures. We would expect the total values to be maximum ones since they assume a quite dirty feed stream and rather conservative design criteria.

Table 18. Surface area requirements for settling basins and reservoirs for SNG plant examples in Four Corners, New Mexico and Campbell County, Wyoming

	Throughput		Settling	Water	Surface Area	
	N.M. (gpm)	WYO. (gpm)	Time (days)	Depth (ft)	N.M. (10^3 ft^2)	WYO. (10^3 ft^2)
Settling Basin	5,700	3,900	1	3	365	250
Reservoir	5,700	3,900	7	21	365	250

Table 19. Water loss rates from evaporation for settling basins and reservoirs in SNG plant examples in Four Corners, New Mexico and Campbell County, Wyoming

	Four Corners, New Mexico (gpm)	Campbell County, Wyoming (gpm)
Settling Basin	36	18
Reservoir	36	18
TOTAL	72	36

The use of greater depths and other design changes would reduce the surface area and hence the loss rate. Furthermore, the application of monomolecular films on the water surface could also greatly suppress the evaporation, at probably a quite reasonable cost because of the relatively large surface areas involved (ref. 36).

We may compare the total evaporation derived for our Four Corners plant with the Fluor-Wesco design by scaling our base throughput from 3,800 gpm to 5,100 gpm. In that case we would arrive at a water loss rate of about 100 gpm compared with 420 gpm for the Wesco plant (ref. 8). Of course, there are undoubtedly a number of design assumptions which account for the difference.

Additional pond evaporation losses are not evaluated since they have, in part, already been taken into account implicitly in the assumed makeup rate for the coal preparation calculations. Other ponding recycle losses are not expected to be large and are not evaluated further here since they are quite specific to the treatment system.

Ash Disposal

The quantity of ash or slag leaving a gasifier that must be disposed of is a function of the ash content of the coal fed to the gasifier. The ash content of the coal in turn depends on the location of the mine from which the coal was taken (see table 16). On the other hand, the process defines the temperature at which the ash or slag leaves the gasifier. This temperature is important for water consumption since the ash or slag must be cooled down before disposal, mainly for reasons of safety. Normally, the cooling is done by quenching with water down to a temperature somewhat below the boiling point, generally around 200° F.

For most coals, ash will begin to deform around 2,000 to 2,500° F and fuse at temperatures about 100° F higher (ref. 37). The temperature in the gasification section of a Lurgi gasifier is between 1,400 and 1,600° F. However, the temperature is moderated at the bottom of the reactor by the steam which is introduced there. As a result, the ash probably leaves at a temperature of from 800 to 1,400° F. On the basis of reasonable assumptions we have deduced from the data on ash disposal given in ref. 23 that a temperature of about 1,000° F appears to have been selected for the design value. In slagging gasifiers, such as Bigas, the slag will be quenched at temperatures closer to 2,700° F. For purposes of our example we shall assume that in disposal the ash is quenched from 1,000° F down to 200° F.

In our example, as outlined in the section on coal washing, 21,860 tons/day of coal is fed to the gasifier. From table 16, the weight percent of ash in the Navajo coal is 26% and that in the Wyoming coal is 8.1%. The product of the coal rate and percent ash gives 5,685 tons/day of ash to be disposed of in our New Mexico example and 1,770 tons/day in the Wyoming example. The rate at which water is evaporated in cooling down the hot ash can be determined from the relation for the rate of heat removal, which in consistent units is given by

heat removed/time = specific heat x temperature drop x ash quenched/time.

Dividing the heat removal rate by the heat of vaporization (1,000 Btu/lb) determines the evaporation rate. Based on the analysis of bituminous ash (ref. 37), we have estimated the ash specific heat to be about 0.2 Btu/lb/° F. Using the estimated temperature drop of 800° F the amount of water evaporated is 152 gpm for the New Mexico example and 47 gpm for the Wyoming example. The figure given for the Four Corners case is essentially the same as cited in refs. 5 and 23, as it should be, since the ash loadings are the same and since we derived our design temperature drop from the data in these references.

The weight of water remaining in the quenched ash is taken to be 30% of the ash weight (ref. 23) or about 284 gpm for Four Corners and 89 gpm for Campbell County. The total water requirement for quenching the gasifier ash is thus 438 gpm and 136 gpm for New Mexico and Wyoming, respectively.

In addition to the gasifier ash, if as in our example, coal-fired boilers are used to generate steam, boiler ash must also be disposed of. In the boilers, about three-quarters of the ash will be removed by wet scrubbing of the stack gases, while the remainder will be removed as bottom ash. We can approximately estimate the amount of consumed water by taking the water requirement per unit weight of ash to be disposed of to be the same as that for the gasifier. In the section on coal washing it was pointed out that 3,760 tons/day of washed Navajo coal was required for the boilers so that on an equivalent heating value basis, 4,104 tons/day of the composite Wyoming coal of table 16 would be needed. The respective ash disposal rates are 530 tons/day for Navajo coal and 332 tons/day for Wyoming coal, with the corresponding rates of consumed water equal to 40 gpm and 25 gpm.

Sludge Disposal

The largest amount of consumed water in the disposal of sludge will be that water remaining in the sludge from the settling basin that is used to remove the suspended solids from the intake feed. The feed water is assumed to enter the settling basin with a sediment concentration of 5,000 mg/1. In addition, since this is good quality water, it is assumed that the sediment sludge will be dewatered to 50% weight solids by centrifuging (ref. 23). Using the estimate of a total mean withdrawal from the feed stream of 3,800 gpm for the New Mexico example and 2,600 gpm for the Wyoming example, it follows that the quantities of water remaining in the sludge will be .005 times the withdrawal or 19 and 13 gpm, respectively.

Other Uses

Included among some other consumptive uses of water cited are domestic and utility potable water for plant and mine use, water for sulfur pelletizing, and steam for cleaning the economizer tubes in coal-fired boilers.

An integrated mine and plant complex of the type described would employ about 1,000 people. We may estimate the potable water usage for domestic supplies, fire water, equipment, and plant washing at about 80 gpd/person. The total requirement is therefore about 56 gpm. However, about 90% of this water will be recovered for reuse so that the consumptive use is quite small amounting to only about 6 gpm.

In ref. 8, a relatively large quantity of water is indicated for boiler tube cleaning—that is, cleaning of the economizer tubes in the stacks of the coal-fired boilers. When steam cleaning is employed, the requirement for this purpose is usually about 2% of the steam generated. The amount of steam generated can be estimated by noting that 3,760 tons/day of 9,780 Btu/lb coal is burnt producing steam at about an 88% efficiency. This is approximately 2.7 x 10^6 lb/hr giving a consumptive water requirement of 108 gpm for boiler tube cleaning, which may be compared with the Wesco design estimate of 200 gpm (ref. 8). However, in our design example we shall not consider this particular use of water since compressed air can also be used for economizer tube cleaning. The tradeoff of capital cost for the compressors against the cost of water will be examined in the ongoing study.

In ref. 8, 250 gpm of water is shown as consumed in pelletizing sulfur. Here again, we shall not consider this use because of the water-short nature of the areas examined and since the sulfur can be shipped either as a liquid or in cast blocks. These costs will also be examined in detail.

Summary of Evaporation, Disposal, and Other Needs

Once more, the importance of site is seen to stand out in determining the water consumed in evaporation, ash, and solids disposal. In table 20 we have summarized these quantities and although the total difference between the two locations is not as dramatic as for mining and reclamation, it is nevertheless quite significant. Again, even the larger of the two totals is seen to be significantly lower than had previously been suggested.

SUMMARY AND CONCLUSIONS

Taking the process net consumption of water equal to 0.8 x 10^6 gal/day, consistent with the Lurgi design (ref. 8), we can then combine this value with the results of the present estimates to present a summary picture of the total consumed water in our illustrative integrated Western mine operations and SNG plants producing 250 x 10^6 scf/day. This summary is given in table 21. It must be emphasized strongly that these results are for the illustrative conditions chosen for the examples of this paper. They should not be taken as representative of all SNG plants nor should they be used to make generalized assessments without further interpretation. In this regard, it is worthwhile mentioning again that even for detailed designs, the consumed water estimates between different process designs at the same location cannot be expected to agree to within better than 20%.

Table 20. Summary of amounts of water consumed in evaporation, solids disposal and other use examples for an SNG plant producing 250 x 10^6 scf/day

	Four Corners, New Mexico		Campbell County, Wyoming	
	(gpm)	(10^6 gal/day)	(gpm)	(10^6 gal/day)
Pond Evaporation	72	0.10	36	0.05
Gasifier Ash Disposal	436	0.62	136	0.19
Boiler Ash Disposal	40	0.06	25	0.04
Sludge Disposal	19	0.03	13	0.02
Other Uses	6	0.01	6	0.01
TOTAL	573	0.82	216	0.31

Table 21. Summary of amounts of water consumed for specific examples of integrated western mine operations and SNG plants producing 250 x 10^6 scf/day

	Four Corners, New Mexico (10^6 gal/day)	Campbell County, Wyoming (10^6 gal/day)
Process, including fuel gas generation	0.80	0.80
Cooling	3.11	2.64
Mining, reclamation	0.77	0.05
Evaporation, solids disposal, other uses	0.82	0.31
TOTAL	5.50	3.80

A principal conclusion which can be drawn from the results is that generalized estimates of water consumption for Western mine-plant complexes to make synthetic natural gas from coal are of limited value, if they are not both site specific and design specific. Another conclusion is that the published water requirements for integrated SNG plants and mine operations in the West may be high and that the actual requirements could, depending on the location, be half the lowest estimate to date.

ACKNOWLEDGMENTS

The present paper summarizes some results from a general study on all aspects of water for synthetic fuel production, including quantity, quality, and treatment. This study is supported by the National Science Foundation under RANN Grant No. SIA74-19080-A01 and the Environmental Protection Agency under Contract No. 68-03-2207. We wish to acknowledge the assistance of Joseph Shen in the preparation of this paper. We also wish to acknowledge the assistance under subcontract of Stone & Webster Engineering Corp. in various aspects of the cooling study reported here. This work was performed by W. D. Comley, C. Jones, and W. Paniciocco.

REFERENCES

1. Federal Energy Administration, Water Resources Task Force, "Project Independence Blueprint-Water for Energy," Report prepared by A. D. Little, Inc., Sept. 5, 1974.

2. U. S. Department of the Interior, Water for Energy Management Team, "Report on Water for Energy in the Upper Colorado River Basin," July 1974.
3. U. S. Department of the Interior, Water for Energy Management Team, "Report on Water for Energy in the Northern Great Plains Area with Emphasis on the Yellowstone River Basin," July 1975.
4. G. H. Davis and L. A. Wood, "Water Demands for Expanding Energy Development," U. S. Geological Survey Circular 703, 1974.
5. El Paso Natural Gas Company, "Second Supplement to Application for Certificate of Public Convenience and Necessity," Federal Power Commission Docket CP73-131, 1973.
6. C. R. Gibson, G. A. Hammons, and D. S. Cameron, "Environmental Aspects of El Paso's Burnham I Coal Gasification Complex," in Proceedings, *Environmental Aspects of Fuel Conversion Technology* (May 1974, St. Louis, Missouri), pp. 91-100, U. S. Environmental Protection Agency, EPA-650/2-74-118, Oct. 1974.
7. J. D. Stracser, "General Facilities Offsite, and Utilities for Coal Gasification Plants," *IGT Symposium on Clean Fuels from Coal*, pp. 639-652, Institute of Gas Technology, Chicago, Ill., Sept. 10-14, 1973.
8. T. E. Berty and J. M. Moe, "Environmental Aspects of the Wesco Coal Gasification Plant," in Proceedings, *Environmental Aspects of Fuel Conversion Technology* (May 1974, St. Louis, Missouri), pp. 101-106, U. S. Environmental Protection Agency, EPA-650/2-74-118, Oct. 1974.
9. Federal Power Commission, *National Gas Survey, Vol. II. Task Force Reports*, Section XII, p. 503, 1973.
10. E. Schmetz, H. Podall, and G. A. Mills, "Water Requirements for a Synthetic Fuels Industry Based on Coal," in Proceedings, *Workshop on Research Needs Related to Water for Energy*, Water Resource Center Publication UILU-WRC-74-0093, University of Illinois at Urbana-Champaign, Nov. 1974.
11. Hittman Associates, "Environmental Effects, Impacts and Issues Related to Large Scale Coal Refining Complexes, Vol. 2," Energy Research and Development Administration R&D Report No. 101 – Interim Report No. 2, (NTIS No. FE-1508-T2), pp. 75-78, May 1975.
12. University of Oklahoma, Science and Public Policy Program, "Energy Alternatives: A Comparative Analysis," pp. 1-113, Univ. of Oklahoma, Norman, Oklahoma, May 1975.
13. A. J. Forney et al., "Analyses of Tars, Chars, Gases, and Water Found in Effluents from the Synthane Process," in Proceedings, *Environmental Aspects of Fuel Conversion Technology* (May 1974, St. Louis, Missouri), pp. 107-113, U. S. Environmental Protection Agency, EPA-650/2-74-118, Oct. 1974.
14. Air Products and Chemicals Inc., "Engineering Study and Technical Evaluation of the Bituminous Coal Research, Inc. Two-Stage Super Pressure Gasification Process," Office of Coal Research R&D Report No. 60, 1971.
15. J. P. Strakey Jr., A. J. Forney, and W. P. Haynes, "Effluent Treatment and Its Cost for the Synthane Coal-to-SNG Process," Am. Chem. Soc., Div. of Fuel Chemistry Reprint Vol. 19, No. 5, p. 94, 1974. (Paper presented at ACS 168th Natl. Meet., Atlantic City, N. J., Sept. 1974).
16. U. S. Department of the Interior, "An Economic Evaluation of SYNTHANE Gasification of Pittsburgh Seam Coal at 1000 psia Followed by Shift Conversion, Purification, Single-Stage Tube Wall Methanation and Pollution Control," Report No. 74-31, Bureau of Mines, Morgantown, W. Va., 1974 (RESTRICTED).
17. C. L. Tsaros, S. J. Knabel, and L. A. Sheridan, "Process Design and Cost Estimate for Production of 265 Million SCF/Day of Pipeline Gas by the Hydrogasification of Bituminous Coal," Office of Coal Research R&D Report No. 22 – Interim Report No. 1, 1965.
18. Transwestern Pipeline Co., Transwestern Coal Gasification Co., Pacific Coal Gasification Co., Western Gasification Co., "Amended Application for Certificate of Public Convenience and Necessity," Federal Power Commission, Docket No. CP73-211, 1973.
19. J. H. Crow and J. R. Dungan, "Hot Potash Process Purifies Gas at Lone Star's Fashing Plant," *Oil & Gas J.*, 97-99, Nov. 24, 1958; also H. E. Benson and J. H. Field, "New Data for Hot Carbonate Process," *Petroleum Refiner*, 39(4):127-132, April 1960; also literature from Benfield Corp., Pittsburgh, Pa.
20. Air Products and Chemicals, Inc., "Feasibility Study of a Coal Slurry Feeding System for High Pressure Gasifiers," Office of Coal Research R&D Report No. 68 (Final), December 1971.
21. G. F. Cavaliere and R. A. Gyepes, "Cost Evaluation of Intercooler Systems for Air Compressors," *Hydrocarbon Process.*, 52(1):107-110, Oct. 1973.
22. M. W. Larinoff and L. L. Forster, "Dry and Wet-Peaking Tower Cooling Systems for Power Plant Applications," Paper presented at ASME Winter Annual Meeting, Houston, Texas, December 1975.
23. Batelle Columbus Laboratories, "Detailed Environmental Analysis Concerning a Proposed Gasification

Plant for Transwestern Coal Gasification Co., Pacific Coal Gasification Co., Western Gasification Co. and The Expansion of a Strip Mine Operation Near Burnham, New Mexico Owned and Operated by Utah International Inc.," Federal Power Commission, Feb. 1, 1973.

24. Atlantic Richfield Co., "Preliminary Environmental Impact Assessment for the Proposed Black Thunder Coal Mine, Campbell County, Wyoming," also "Revised Mining and Reclamation Plan for the Proposed Black Thunder Coal Mine, Campbell County, Wyoming," Denver, Colorado, 1974.

25. Atlantic Richfield Co., "Black Thunder Mine, 10 Million Ton Per Year Water Supply," (Personal communication, Hugh W. Evans), Denver, Colorado, March 6, 1975.

26. National Academy of Sciences, *Rehabilitation Potential of Western Coal Lands*, p. 168, Ballinger Publishing, Cambridge, Mass., 1974.

27. Utah International Inc., "UII Water Requirements for Fluor Wesco Lurgi Plant," (Personal communication, L. E. McCloskey), San Francisco, Cal., Oct. 3, 1975.

28. D. H. McCrea and J. H. Field, "The Purification of Coal Dervied Gases: Applicability and Economics of Benfield Processes," Paper No. 29b, AIChE 78th Natl. Meeting, Salt Lake City, Utah, August 1974.

29. Northern Great Plains Resources Program, Mineral Resources Work Group, Discussion Draft, Feb. 1974.

30. J. W. Leonard and D. R. Mitchell (editors), *Coal Preparation*, pp. 17-5, 17-6, Am. Inst. of Mining, Metallurgical, and Petroleum Engineers, New York, 1968.

31. Proceedings, *Second Research and Applied Technology Symposium on Mined-Land Reclamation*, Oct. 22-24, 1974, National Coal Association, Washington, D.C., 1974.

32. Proceedings, *Third Symposium on Surface Mining and Reclamation, Vol. I*, Oct. 21-23, 1975, National Coal Association, Washington, D.C., 1975.

33. F. E. Aldon, "Techniques for Establishing Native Plants on Coal Mine Spoils in New Mexico," in Proceedings, *Third Symposium on Surface Mining and Reclamation, Vol. I*, pp. 21-28, National Coal Association, Washington D.C., 1975.

34. R. L. Tresler, "Strip Mine Reclamation in Wyoming," in Proceedings, *Second Research and Applied Technology Symposium on Mined-Land Reclamation*, pp. 22-28, National Coal Association, Washington, D.C., 1974.

35. T. Yamamoto, "Coal Mine Spoils as a Growing Medium: Amax Belle Ayr South Mine, Gillette, Wyoming," in Proceedings, *Third Symposium on Surface Mining and Reclamation, Vol. I*, pp. 49-61, National Coal Association, Washington, D.C., 1975.

36. Office of Water Resources Research, "Evaporation Suppression, A Bibliography," WRSIC Report No. 73-216, (NTIS No. PB-231-200), U. S. Dept. of the Interior, Washington, D.C., Dec. 1973.

37. T. A. Hendrickson (ed.), *Synthetic Fuels Data Handbook*, Cameron Engineers, Inc., Denver, Colorado, 1975.

38. R. N. Maddox, *Gas and Liquid Sweetening*, p. 57, John M. Campbell and Co., 1974.

39. R. F. Neerken, "Compressor Selection for the Chemical Process Industries," *Chem. Engineering*, 82(2):78-94, Jan. 20, 1975.

40. Elliott Division Carrier Corp., "Elliot Multistage Compressors," Bulletin, p. 25, 1973.

41. F. C. Riesenfeld and A. L. Kohl, *Gas Purification*, 2nd ed., p. 485, Gulf Publishing Co., 1974.

APPENDIX

REPRESENTATIVE FORMULAE AND DATA USED FOR CALCULATING COST OF WET AND DRY COOLING

1. Heat Transfer Coefficients (U)

		U, Btu/(hr)(ft^2)(° F)*	
		Dry	Wet
Condensing steam from turbine drives		130	400
Condensing steam in the presence of noncondensible gases in gas purification regenerator (ref. 38)		75	110
Cooling methane at 1,000 psig		70	100
Cooling water for off-gas scrubbing		120	170
Air and oxygen compressor interstage coolers	psig		
	10	10	12
	50	20	20
	100	30	40
	300	40	50
	>500	50	70

---

*Unfinned area for dry coolers.

2. Heat Transfer Area

(a) Dry cooling

The following empirical formula for the air temperature rise was used

$$\Delta t = 0.005\,U\left[\frac{T_1 + T_2}{2} - t_1\right].$$

Here, t_1 is the inlet air temperature and T_1, T_2 are the process stream inlet and outlet temperatures. The other formulae for calculating the heat transfer area are standard.

(b) Wet cooling

Standard formulae were used with assumed cooling water temperatures of 80° F cold and 105° F hot.

3. Compressor Formulas

These may be found, for example, in refs. 39 and 40. The polytropic efficiency was taken to be 77 percent.

4. Energy for Cooling

Dry cooler fans

Horsepower = 0.015 X Area ($U < 50$)
= 0.0175 X Area ($50 \leq U < 100$)
= 0.02 X Area ($U \geq 100$)

Cooling tower fans

Horsepower = 0.012 X gpm circulated

Cooling water circulation pumps

Horsepower = 0.03 X gpm circulated

5. Costs

Area	Cost	Pressure (p, psig)
Dry cooling	\$ 18/ft^2	
Wet cooling	\$5.1/ft^2	$p<300$
	\$5.6/ft^2	$300 \leq p < 450$
	\$6.1/ft^2	$450 \leq p < 600$
	\$6.9/ft^2	$p \geq 600$

Other	
Cooling tower	\$7/gpm circulated
Compressors	\$135/hp
Electrical energy	2.24¢/hp-hr (3¢/kWh)
Steam	\$3/10^6 Btu

SULFUR EMISSION CONTROLS FOR A COAL GASIFICATION PLANT

Milton R. Beychok*

Abstract

Through a summary of the WESCO coal gasification project, an example of environmentally sound fuel conversion technology is presented. It is proposed that first generation gasification plants will be predominantly of the Lurgi type.

The following recommendations are made concerning sulfur control regulations specific to coal gasification processes:

- *The regulations should* *not* *be in terms of concentration.*
- *Carbonyl sulfide emissions should not be excused. The regulations should include all sulfur species.*
- *The burning of coal, oil, and gas in the auxiliary steam boilers and superheaters is already covered by existing EPA regulations. The gasification plant regulations should* *not* *include those auxiliaries.*
- *An acceptable and equitable regulation might be:*

  > *THE TOTAL EMISSION OF ALL SULFUR SPECIES IN ALL VENTS AND STACKS FROM A COAL GASIFICATION PLANT (EXCLUDING ANY STEAM GENERATION FACILITIES) SHOULD NOT EXCEED 1.5-3.0 PERCENT OF THE SULFUR CONTAINED IN THE GASIFIER FEEDSTOCK COAL.*

I very much appreciate this opportunity to present an industry viewpoint on the control of sulfur emissions from coal gasification plants. Later in this presentation, I will discuss the detailed sulfur control features of an actual design for a full-scale commercial coal gasification project. But first I would like to talk for a few minutes on how industry and the EPA might improve their working relationship. There would be far less court litigation between industry and the EPA if industry could effectively participate in developing emission control regulations—and if industry viewpoints were truly given serious consideration. I fully realize that some industry viewpoints are nonproductive and perhaps overly opposed to meaningful regulations. But the large majority of industry is willing to accept emission regulations based upon realistic data and commercially proven technology. The EPA should solicit industry viewpoints very early in their process of developing regulations, and provide industry a real opportunity to participate in their decisionmaking. It is not enough merely to invite formal written comments within a legalistic time limit of 30 or 60 days after publication of a background document or proposed promulgations—especially when those documents or proposed promulgations represent months or years of work and many irreversible decision steps by the EPA and their contractors. What industry wants is early participation, face-to-face dialogues, and a meaningful opportunity to help formulate proposed regulations through all the stages of decisionmaking. I submit that a working partnership between industry and the EPA would drastically reduce the court litigation involving emission regulations.

In considering the regulation of emissions from an emerging industry such as coal gasification, we must first determine what process technology that emerging industry will utilize. There are at least ten full-scale commercial coal gasification projects currently proposed and seriously under design or study in the United States. They include the following:

Location	Owner
New Mexico	WESCO (Western Gasification Co.)
New Mexico	EPNG (El Paso Natural Gas)
North Dakota	Natural Gas Pipeline Co.
North Dakota	ANG (American Natural Gas)
Wyoming	Panhandle Eastern
Wyoming	Cities Service
Illinois	Texas Eastern Transmission
Kentucky	Texas Gas Transmission
Montana	Burlington Northern
Utah	(Confidential)

All but perhaps one or two of these plan to use Lurgi coal gasification technology. The WESCO and EPNG projects in New Mexico and the ANG project in North Dakota have filed for regulatory approval with the Federal Power Commission (FPC)—and some of the other projects plan to file with the FPC fairly soon. The WESCO project has already obtained a very favorable FPC ruling and fully expects final approvals. WESCO has also obtained permit approval from the New Mexico Environmental Improvement Agency and the New Mexico Surface Mine Commission, and the final WESCO EIS will soon be issued by the Department of Interior. The plant is fully designed and major equipment specifications are ready for purchase. By all standards, the WESCO project is the most advanced of all the coal gasification projects. All that is needed for the WESCO project to start construction tomorrow is government assistance with financing for coal gasification plants producing high-Btu pipeline gas. There can be little doubt that the first generation of coal gasification plants will use Lurgi gasification technology.

---

*The author is a consulting engineer in Irvine, California.

Another consideration in developing regulations for an emerging industry is how to obtain a realistic basis for such regulations. When developing standards for an existing industry, the EPA first examines existing plants to determine the emission abatement levels attained in "exemplary" plants. Since we have no exemplary plants in the emerging coal gasification industry, we can only examine "exemplary" designs. This brings me to my first major point:

> **The EPA should recognize that the first-generation coal gasification plants will most probably use Lurgi technology. The EPA should develop regulations specific to Lurgi technology and should base those regulations on the "exemplary" designs of WESCO, EPNG, and ANG.**

In my opinion, the WESCO, EPNG, and ANG exemplary designs are much more meaningful than any "paper" designs that could be or have been developed by any EPA contractor. Having been with the WESCO project for almost 5 years, I know that millions of dollars have been spent to bring that design and project to its current status. An EPA contractor limited to $100,000 or $200,000 of funding could never hope to equal the design expertise expended on the WESCO project.

It is also my opinion that the EPA should not dilute their efforts by attempting at this time to develop regulations that would include the many second-generation gasification processes under development in the United States by ERDA, the American Gas Association, Bituminous Coal Research, the Institute of Gas Technology, and others. When and if the second-generation demonstration plants funded by ERDA have been proven successful, the EPA will have access to their operating data and could then develop emission regulations for the subsequent commercial exploitation of the second-generation processes. This brings me to my next major point:

> **The EPA should develop regulations specific to second generation coal gasification processes after the ERDA demonstration plants have shown which of those processes will truly be commercially viable.**

This recommendation is perfectly consistent with the existing EPA policy of developing regulations specific to process categories within a given industry. For example, the EPA's effluent guidelines for the petroleum refining industry are divided into five sets of guidelines for five categories of refinery process arrangement. As another example, the NSPS for lead smelters (40 CFR 60, Subpart L) specifies different emission standards for reverberatory furnaces than for pot furnaces; thus it would be quite consistent for the EPA to:

- First develop coal gasification emission regulations for the first generation Lurgi technology based on the available exemplary designs.
- Then develop regulations for the second-generation coal gasification plants based on operating data from the ERDA-funded demonstration plants.

In my opinion, the Booz-Allen report, contracted by the EPA to develop a data base for coal gasification sulfur emission regulations, encompassed too broad a scope by including first and second generation plants. As noted earlier, a $100,000-200,000 report could not hope to do an adequate study of Lurgi technology alone–and it certainly couldn't do an adequate study of the many first and second generation processes as the Booz-Allen report attempted to do.

WESCO DESIGN AND RATIONALE

Now, let us examine the sulfur emission control design for the WESCO project and the rationale for the design. But first I want to emphasize that the WESCO design is based on meeting the gasification emission standards developed by the State of New Mexico, which are the only such standards yet promulgated in the United States. The auxiliary coal-fired steam boiler in the WESCO design is also based on meeting the New Mexico regulations for coal combustion which are far more stringent than the EPA's standards for coal combustion. If I may digress for a moment and refer back to my opening remarks about letting industry participate in developing regulations, the New Mexico coal gasification regulations are an outstanding example of such cooperation. In late 1971, WESCO was asked by New Mexico to assist them in developing regulations and WESCO responded affirmatively. The New Mexico EIA and WESCO worked together over a period of many months to hammer out a set of draft regulations. The draft was then reviewed in depth at a public meeting of the New Mexico EIA's Technical Advisory Committee which included representatives of local environmentalist organizations. A redrafted version was then reviewed at a public hearing before the New Mexico Environmental Improvement Board, and a final version was subsequently adopted into law in September 1973. The final version was not completely in agreement with WESCO's original suggestions, but it was accepted and implemented in WESCO's plant design. When WESCO submitted their design along with a permit application, the New Mexico EIA granted a permit and approval to construct. As of today, there has been no litigation and no appeal either by industry or by the strong local environmentalist organizations. All in all, it was a story of excellent cooperation between industry and the State EIA.

Now, let me explain the WESCO sulfur emission control design (see figure 1). For those of you who may not be familiar with coal gasification to produce high-Btu pipeline gas, the key processing steps are those within the bold outlines on the flow sheet (figure 1):

Gasifiers – pressure vessels where coal, steam, and oxygen are reacted to yield a crude gas containing methane, hydrogen, carbon oxides, excess steam, and various byproducts and impurities. About 40% of the plant's ultimate methane (SNG) product is produced here. Subsequent reaction steps produce the other 60%.

Shift Conversion – excess carbon monoxide in the crude gas is catalytically converted ("shifted") to carbon dioxide to provide the 3-to-1 hydrogen-to-carbon monoxide ratio required for additional methane synthesis in the subsequent methanation step.

Rectisol Gas Purification – the Rectisol absorption process, using refrigerated methanol, selectively removes hydrogen sulfide and carbon dioxide from the crude gas. Precooling at the Rectisol process entry recovers byproduct naphtha.

Methanation – hydrogen and carbon monoxide (in a 3-to-1 ratio) are catalytically combined to form methane and byproduct water. About 60% of the end product methane (SNG) is produced here, and a final Rectisol scrub removes any residual carbon dioxide.

The gasifier feedstock coal contains 226.4 tons/day of sulfur. About 5% (11.3 tons/day) of that remains in the byproduct tars, oils, and naphtha and the remaining 95% (215.1 tons/day) is gasified. About 2.19 tons/day of the gasified sulfur are in the form of carbonyl sulfide (COS) and the remaining 212.91 tons/day are in the form of hydrogen sulfide.[*] Thus about 94% of the coal sulfur appears as gasified H_2S and about 1% appears as COS. Since the emission control of COS is somewhat more difficult than the control of H_2S, it is important to define the amount of COS produced during gasification when comparing different designs.

As shown in figure 1, some of the gasified sulfur distributes among seven minor gas streams, but most of it (202.9 tons/day) remains with the crude product gas entering the Rectisol unit. As noted earlier, the Rectisol unit removes sulfur and carbon dioxide from the crude gas. Most of the sulfur (141.8 tons/day) is removed as a rich-H_2S gas stream containing roughly 21 vol % H_2S. Another lean-H_2S gas stream contains roughly 0.9 vol % H_2S (61.1 tons/day of sulfur). The lean-H_2S stream is much larger than the rich-H_2S stream because it contains about 8,800 tons/day of CO_2 while the rich-H_2S stream has only about 700 tons/day of CO_2.

The small rich-H_2S stream would be ideally suited for routing through a Claus unit which converts H_2S into byproduct sulfur—but it contains more hydrocarbons (38 tons/day) than a Claus unit can tolerate. The large lean-H_2S stream (0.9 vol % H_2S) is much too lean for a Claus unit and yet contains more sulfur (61.1 tons/day) than point source regulations would permit releasing to the air—as well as 94 tons/day of hydrocarbons which, if released to the atmosphere, would create serious difficulty in meeting the ambient air quality standards (AAQS) for hydrocarbons. Incineration of the lean-H_2S stream would eliminate the hydrocarbon problem but would still release the sulfur to the atmosphere as sulfur dioxide. In order to solve the problems of point-source sulfur emissions and ambient air quality hydrocarbon standards, the WESCO design does the following:

- The small rich-H_2S stream is further treated in a second gas purification unit for the selective separation of hydrocarbons (shown as an "H_2S-concentrator" in figure 1). The resultant enriched-H_2S stream contains about 70 vol % H_2S and is ideally suited for routing through the Claus unit along with one of the minor gas streams (from naphtha separation within the Rectisol unit). The Claus unit will convert 95% of this H_2S to byproduct sulfur.
- The large lean-H_2S stream and the offgas from the phenol extraction unit are routed through Stretford units for essentially complete conversion of their H_2S to byproduct sulfur (98.6% conversion). However, the lean-H_2S stream contains about 0.9 tons/day of sulfur as COS which is not converted in a Stretford unit.
- The Claus unit tail gas, the Stretford unit tail gas, the hydrocarbons from the H_2S-concentrator, and other minor gas streams are all incinerated in the steam boiler fireboxes. This converts their 12.3 tons/day of residual sulfur species to SO_2 and prevents any hydrocarbon emissions. The resultant SO_2 is then removed at

---

[*] All sulfur quantities on figure 1 (including COS) are expressed as tons/day of elemental sulfur. Also, the "all sulfur species" quantities include the COS quantities—they are not cumulative.

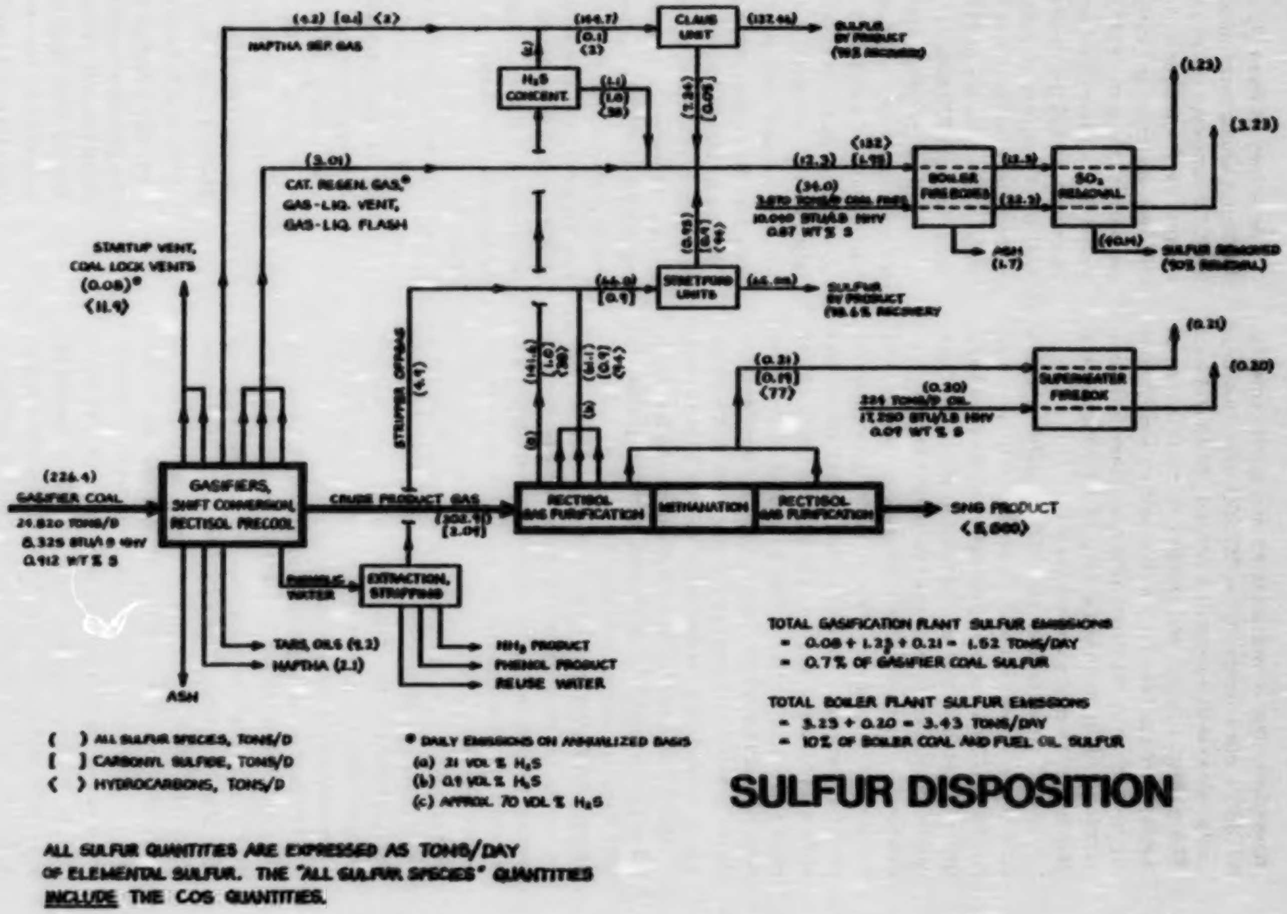

(4.2) [0.1] ⟨2⟩
NAPTHA SEP. GAS
(164.7)
[0.1]
⟨2⟩
CLAUS UNIT
(132.46)
SULFUR BY PRODUCT (96% RECOVERY)
(b)
H2S CONCENT.
(1.1)
[1.0]
⟨38⟩
(1.84)
[0.05]
(3.01)
CAT. REGEN. GAS,*
GAS-LIQ. VENT,
GAS-LIQ. FLASH
⟨132⟩
(12.3)
[1.75]
(34.0)
3,870 TONS/D COAL FIRED
10,000 BTU/LB HHV
0.87 WT % S
BOILER FIREBOXES
(12.3)
(32.3)
SO2 REMOVAL
(1.23)
(3.23)
ASH
(1.7)
(40.14)
SULFUR REMOVED
(90% REMOVAL)
(0.75)
[0.7]
⟨96⟩
STARTUP VENT,
COAL LOCK VENTS
(0.08)*
⟨11.9⟩
(44.0)
[0.9]
STRETFORD UNITS
(46.00)
SULFUR BY PRODUCT
(98.6% RECOVERY
STRIPPER OFFGAS
(4.9)
(141.4)
[1.0]
⟨38⟩
(a)
(33.1)
[0.9]
⟨94⟩
(c)
(0.21)
[0.19]
⟨77⟩
(0.20)
224 TONS/D OIL
17,250 BTU/LB HHV
0.07 WT % S
SUPERHEATER FIREBOX
(0.21)
(0.20)
(226.4)
GASIFIER COAL
24,820 TONS/D
8,325 BTU/LB HHV
0.912 WT % S
GASIFIERS,
SHIFT CONVERSION,
RECTISOL PRECOOL
CRUDE PRODUCT GAS
(202.9)
[2.04]
RECTISOL GAS PURIFICATION
METHANATION
RECTISOL GAS PURIFICATION
SNG PRODUCT
⟨5,000⟩
PHENOLIC WATER
EXTRACTION, STRIPPING
TARS, OILS (9.2)
NAPTHA (2.1)
ASH
NH3 PRODUCT
PHENOL PRODUCT
REUSE WATER
( ) ALL SULFUR SPECIES, TONS/D
[ ] CARBONYL SULFIDE, TONS/D
⟨ ⟩ HYDROCARBONS, TONS/D
* DAILY EMISSIONS ON ANNUALIZED BASIS
(a) 21 VOL % H2S
(b) 0.1 VOL % H2S
(c) APPROX. 70 VOL % H2S
TOTAL GASIFICATION PLANT SULFUR EMISSIONS
= 0.08 + 1.23 + 0.21 = 1.52 TONS/DAY
= 0.7% OF GASIFIER COAL SULFUR
TOTAL BOILER PLANT SULFUR EMISSIONS
= 3.23 + 0.20 = 3.43 TONS/DAY
= 10% OF BOILER COAL AND FUEL OIL SULFUR
SULFUR DISPOSITION
ALL SULFUR QUANTITIES ARE EXPRESSED AS TONS/DAY
OF ELEMENTAL SULFUR. THE "ALL SULFUR SPECIES" QUANTITIES
INCLUDE THE COS QUANTITIES.

Figure 1. Sulfur disposition

90% efficiency in the boiler stack gas scrubbers.

- The final Rectisol offgas (containing about 8,000 tons/day of CO_2, 0.21 tons/day of sulfur and 77 tons/day of hydrocarbons) is incinerated in the steam superheater firebox. This prevents any hydrocarbon emissions and the small amount of resultant SO_2 does not require removal.

The net result (as shown in figure 1) is that the total gasification plant sulfur emissions amount to only 0.7% of the sulfur in the total gasifier coal feedstock. This excellent control is achieved by incinerating the tail gases from the primary sulfur recovery units (Claus and Stretford) which converts any residual sulfur species into SO_2 that is then removed in the boiler stack gas scrubbers. Thus, even the COS which is not converted in the Stretford units (or from any other source) is removed after incineration to SO_2.

Table 1 (emissions vs. regulations) illustrates how the gasification plant sulfur emissions will meet the New Mexico regulations. It also illustrates how the emissions from fuel combustion in the steam boilers and superheaters will better the New Mexico regulations which are 2-3 times more stringent than the Federal regulations.

This design exemplifies a number of points which are germane to any proposed EPA regulations:

1. The problem of point-source sulfur emission control is interrelated with the prevention of hydrocarbon emissions in amounts that would violate the ambient air quality standards. They cannot be solved independently of each other.
2. Carbonyl sulfide emissions can be prevented by incineration followed by SO_2 removal, and incineration is quite probably required in order to control hydrocarbon emissions.

Table 1. Emissions vs, regulations

Gasifier Coal Heating Value
= (24,820) (2000) (8,325)
= 413,253 x 10^6 Btu/day

Gasification Plant Sulfur Emissions
= 0.08 + 1.23 + 0.21
= 1.52 tons/day
= (1.52) (2000)/413,253
= 0.0074 pounds/10^6 Btu (New Mexico regulation = 0.0080)

Boiler Plant Coal Fines Heating Value
= (3,870) (2000) (10,040)
= 77,710 x 10^6 Btu/day

Boiler Plant SO_x Emissions (from coal-firing)
= (3.23) (2)
= 6.46 tons/day
= (6.46) (2000)/77,710
= 0.166 pounds/10^6 Btu (New Mexico regulation = 0.340)
(Federal regulation = 1.20)

Superheater Fuel Oil Heating Value
= (224) (2000) (17,250)
= 7,728 x 10^6 Btu/day

Superheater SO_x Emissions (from oil-firing)
= (0.20) (2)
= 0.40 tons/day
= (0.40) (2000)/7,728
= 0.104 pounds/10^6 Btu (New Mexico regulation = 0.340)
(Federal regulation = 0.80)

---

3. The number and diversity of gas streams (13 are shown in figure 1) cannot be simplified into a single regulation expressed as point-source concentration in ppm. Also, the common use of stack gas SO_2 scrubbers for the boiler plant flue gases and the gasification residual tail gases complicates the problem. If the regulation is expressed as concentration in ppm, it will cause a great many problems of interpretation regarding common stacks, common scrubbers, and how to "average" the various exit gas streams. It might also encourage plant designers to take advantage of CO_2 or N_2 dilution or excess combustion air in any number of ways.

Table 2 summarizes my recommendations regarding coal gasification sulfur control regulations, and I urge you to give them serious consideration:

- The regulations should not be in terms of concentration.
- Carbonyl sulfide emissions should not be excused. The regulations should include all sulfur species.
- The burning of coal, oil, and gas in the auxiliary steam boilers and superheaters is already covered by existing EPA regulations. The gasification plant regulations should not include those auxiliaries.
- An acceptable and equitable regulation might be:

  The total emission of all sulfur species in all vents and stacks from a coal gasification plant (excluding any steam generation facilities) should not exceed 1.5–3.0 percent of the sulfur contained in the gasifier feedstock coal.

The 1.5-3.0% should be subcategorized for regional differences in coal sulfur contents. Thus, low-sulfur coals might be limited to 1.5% emission and high-sulfur coals to 3.0% emission. This would provide an equalizing incentive to gasify high-sulfur Eastern coals. Otherwise, our large energy reserves of Eastern coal might not be utilized. In any case, even a 3% emission of sulfur in gasification is only one-tenth of the sulfur emitted by an equivalent coal-burning power plant.

CLOSING

In closing, I want to emphasize two caveats concerning my presentation. First, I do not and cannot speak for

Table 2. Recommendations

1. Regulations should not be in terms of concentrations (i.e., ppm by volume).
2. Regulations for gasification should not include auxiliary steam boilers and superheaters. Burning of coal, oil, and gas in steam plants is covered by existing EPA regulations.
3. The gasification plant regulations should include all sulfur species from all vents and stacks (including annualized intermittent operations).
4. Carbonyl sulfide emissions should not be "excused."
5. Recommended wording for high-Btu gasification regulation:

   "THE TOTAL EMISSION OF ALL SULFUR SPECIES IN ALL VENTS AND STACKS FROM A COAL GASIFICATION PLANT (EXCLUDING ANY STEAM GENERATION FACILITIES) SHOULD NOT EXCEED 1.5–3.0 PERCENT OF THE SULFUR CONTAINED IN THE GASIFIER FEEDSTOCK COAL"

   The 1.5–3.0% should be subcategorized for regional differences in coal sulfur contents. Thus, low-sulfur coals might be limited to 1.5% emission and high-sulfur coals to 3% emission.

the entire energy industry. All of my remarks and opinions are based on my involvement with the specific WESCO design to meet the New Mexico regulations. Secondly, I should explain my recommended 1.5–3.0 % emission limit in contrast to WESCO's design limit of 0.7% as shown in figure 1. As an engineer who has spent a lifetime in the process design of industrial plants, I can assure you that the difference between 0.7% and 1.5% is a realistic hedge against the difference between design expectations and actual plant performance.

Finally, I want to thank you for giving me the opportunity to make this presentation. And I want to assure you that most of us in industry share with you a real concern for the integrity of our environment. I am sure that we can both accomplish much more by listening to each other than by shouting at each other.

LOW ENERGY GAS RETROFIT TO INDUSTRY

D. A. Ball*

Abstract

Low- or intermediate-energy gas from coal (with a heating value of 150 to 400 Btu/scf) is an alternate fuel for industries faced with reduced availability of natural gas and an uncertain fuel oil supply. Such a gas can be produced and cleaned of such contaminants as particulates, sulfur, and nitrogen compounds using commercially available technology.

This paper describes conversion of two hypothetical industrial plants (a petroleum refinery, and a secondary steel mill) to onsite production of low- and intermediate-energy gas from coal as a source of process energy. Specific gasifier and gas cleanup equipment requirements are discussed for the hypothetical plants, considering such factors as peak plant load, assumed coal source, and process and piping requirements. The possibility of utilizing existing plant piping and gas burners is discussed. General material and energy flows are presented. The potential environmental impact of conversion to gas from coal is also discussed in terms of emissions from both the gasification process and the combustion process.

INTRODUCTION

In recent years, American industry has been faced with an acute shortage of natural gas as a source of energy. As a result, many industries have become increasingly reliant on oil and propane, substitutes that are easiest to utilize minimum equipment modifications. However, increased demand for these alternate fuels—along with limited supply and foreign politics—have resulted in their cost increasing dramatically and the availability being uncertain.

Table 1 shows the dependence of industry on natural gas and petroleum. In 1973 industry consumed approximately 15.9 Quads (10^{15} Btu) of natural gas and petroleum to satisfy 70 percent of its total energy requirement of 22.9 Quads.

Projections of the future supply of natural gas and oil vary. Figure 1 shows a recent projection of domestically produced natural gas. This projection shows that, with stimulation techniques, supplies of natural gas may improve somewhat in the near future. However, many of these techniques are unproven and their use would result in higher costs of recovering gas. Expensive LNG imports will also aid supply; but, over the next 40 years, consensus is that natural gas will all but disappear as a significant energy source in the United States. Either through allocation or increased price this fuel will become less attractive to industry at a much earlier date.

Oil and propane have been in somewhat greater supply to industry than natural gas, though at higher prices. Much of this supply, however, has been satisfied by foreign imports. In the future, the U. S. government will undoubtedly place increased pressure on reducing these imports to improve its balance of payments position. However, the projection of domestic production of oil, shown in figure 2, would predict a steadily decreasing supply of this fuel. Therefore, oil will probably be more expensive and less available to industry in the future, especially as it is used more heavily as a substitute for natural gas.

One proposed alternate source of energy for industry has been low- or intermediate-energy gas produced from coal. Commercial processes for producing this gas were used widely in American industry over 50 years ago and, although only a few commercial applications remain in this country today, many are still being used in various foreign countries.

Low-energy gas with a heating value of 120 to 200 Btu per standard cubic foot (using air and steam for gasification) and intermediate-energy gas with a heating value of 280 to about 400 Btu per standard cubic foot (using oxygen and steam for gasification) could conceivably be generated onsite and substituted for natural gas and oil in industrial fuel using processes. Such a substitution, however, involves many considerations such as environmental effects, gas distribution, process and burner modification, and economics.

The objective of this study was to evaluate these considerations and their implications for two selected

Table 1. Energy use in industry (ref. 1)

	Quads	Percent
Natural Gas	10.4	46
Petroleum	5.5	24
Coal	4.6	20
Electric	2.4	10

---

*The author is with Battelle's Columbus Laboratories, Columbus, Ohio.

Preceding page blank

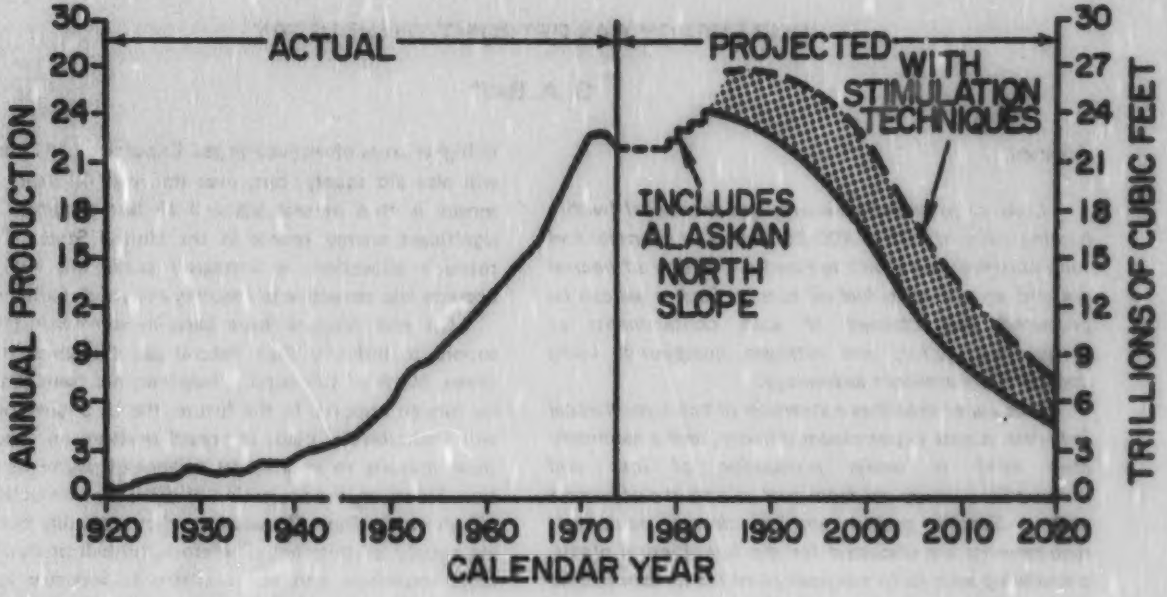


Figure 1. Natural gas projection (ref. 1).

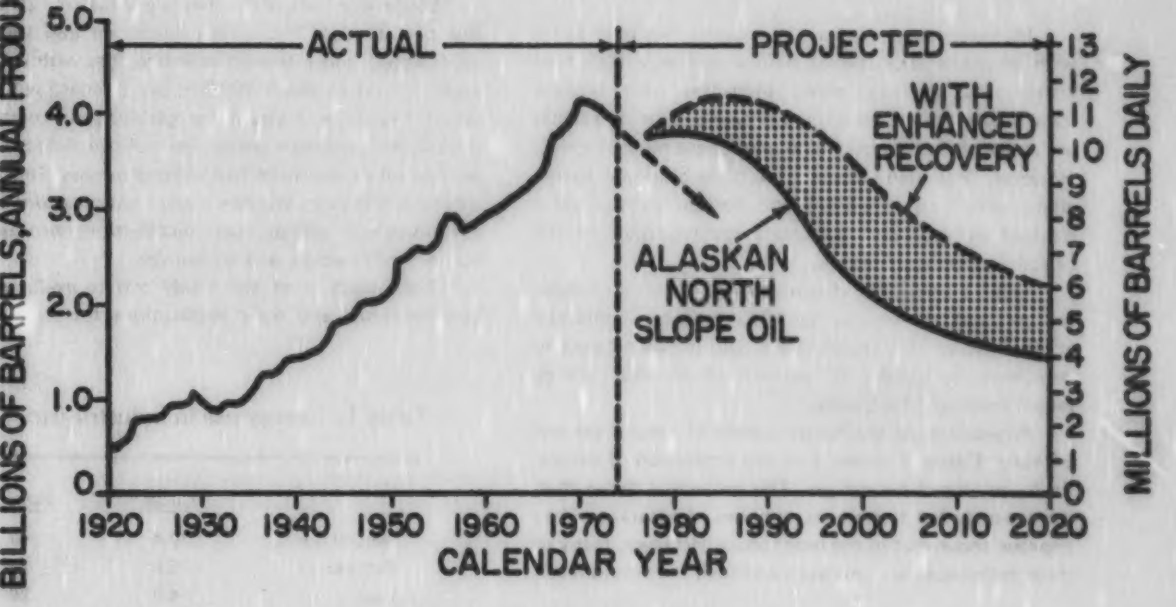


Figure 2. Oil projection (ref. 1).

industries. Selection of the two industries was based on a preliminary analysis of their relative attractiveness and potential for being retrofitted to low- or intermediate-energy gas. Model plants were selected for analysis in each of the two industries. A suitable gasification-gas cleaning system was then selected for each of the two model plants. Material and energy balances were calculated for each gasification plant based on their generating sufficient low- or intermediate-energy gas to satisfy the energy requirements of the model plants. Analysis was then made of the potential environmental impact of such a retrofit and the modifications necessary in the plant fuel distribution and fuel using processes. This paper will deal primarily with the potential environmental effects of such a retrofit.

INDUSTRY SELECTION

The major criterion used in selecting candidate industries for study was existing use of natural gas and oil by 4-digit SIC code. Table 2 shows the 10 top consumers of natural gas, oil, and coal in the United States in 1971 along with their relative ranking in use of these three fuels and amounts of the fuels consumed.

These industries were then evaluated according to other criteria such as amenability of processes to conversion to low- or intermediate-energy gas, location of the industry relative to supplies of coal, and dependence on a supply of gaseous fuel or inability to convert to direct use of coal. Finally, the basic iron and steel industry (SIC 3312) and the petroleum refining industry (SIC 2911) were selected for study.

Basic Iron and Steel Industry

The basic iron and steel industry was subdivided into two parts: integrated mills and secondary mills. Integrated mills are generally large mills that produce steel from raw iron ore by reducing the ore to iron in a blast furnace using coke. This is followed by conversion of the iron to steel, primarily by the Basic Oxygen Process. Because these processes produce significant quantities of waste fuels—particularly the blast furnace and coking operation, integrated steel mills are not as dependent on oil and natural gas as other types of steel

Table 2. Energy use by the 10 major industrial consumers of gas, oil, and coal by 4-digit SIC codes for 1971 (ref. 2)

SIC	Description	Ranking			Energy use 10^{11} Btu/year[a]				
		Gas	Oil	Coal	Gas	Oil	Coal	Total[b]	Total[c]
3312	Blast furnaces and steel	2	1	3	65[illegible]	167	133	953	1254
2818	Industrial organic chemicals (not elsewhere classified)	3	10	4	605	26	132	763	908
3241	Hydraulic cement	5	5	1	208	41	180	429	429
2621	Paper mills	6	2	2	201	161	149	511	526
2631	Paperboard mills	7	3	5	181	157	82	420	436
2911	Petroleum refining	1	4	-	1332	68	9	1409	1440
2819	Industrial inorganic chemicals (not elsewhere classified)	4	-	-	375	23	35	433	453
3334	Primary aluminum	8	-	-	125	1	16	142	143
3221	Glass containers	9	-	-	120	9	-	129	130
3352	Aluminum rolling and drawing	10	-	-	61	2	3	66	72
2821	Plastics and resins	-	7	10	54	29	37	120	134
2611	Pulpmills	-	6	-	38	38	4	80	81
2815	Cyclic intermediate and crudes	-	8	-	13	28	72	113	126
2824	Organic fibers (noncellulosic)	-	9	8	42	26	60	128	132
2812	Alkalies and chlorine	-	-	6	47	4	80	131	139
2823	Manmade fibers (cellulosic)	-	-	7	12	2	64	78	80
3313	Electrometallurgical products	-	-	9	2	1	51	54	56

[a] Gas at 1038 Btu/scf; Oil at 6.0×10^6 Btu/42 gallon barrel; Coal at 26.2×10^6 Btu/short ton.

[b] Total of purchased fossil (gas, oil, coal).

[c] Total of all purchased fuels.

mills or other industries. Secondary mills, on the other hand, have no blast furnaces or coking facilities and produce steel from iron and steel scrap, primarily in electric-arc furnaces. These mills are somewhat smaller but more numerous than integrated mills and are heavily dependent on natural gas and petroleum products for fuels. A recent survey (ref. 3) revealed that a sample of integrated steel mills were only 18.4 percent dependent on natural gas and only 26.3 percent dependent on natural gas and petroleum products combined; secondary steel mills were 65.8 percent dependent on natural gas and 76.3 percent dependent on natural gas and petroleum products combined.

It was estimated that 22 percent of the natural gas and petroleum products used by the basic iron and steel industry (SIC 3312) were consumed in secondary mills. Also, it was estimated that 70 percent of secondary mill capacity is located in the 20 major coal producing and coal bearing states.

Fuel use in secondary steel mills is similar to that in integrated mills and consists of heating large pieces of metal in a variety of furnaces for forming and heat treating operations. Other significant fuel uses include boilers and space heating. In preliminary analysis, these processes were considered relatively amenable to conversion to low- or intermediate-energy gas.

Petroleum Refining Industry

The refinery industry (SIC 2911) is by far the top industrial consumer of natural gas for fuel, consuming about twice as much as the next major consumer, basic iron and steel (SIC 3312). In 1973 natural gas accounted for about 36.1 percent of energy consumed in refinery operations and oil accounted for an additional 11.4 percent (ref. 4). An additional 35.1 percent of refinery energy consumption was satisfied by off-gases from refinery processes. This so-called refinery gas—consisting primarily of methane, ethane, butane, propane, and hydrogen, is a high-grade gas mixture and could potentially be classed as a premium fuel and sold.

Fuels consumed in refinery operations are primarily for feedstock heating in process heaters and steam raising in boilers. Although refineries vary considerably in type and size, the fuel-consuming processes (process heaters and boilers) are relatively uniform in characteristics and on preliminary analysis were considered relatively amendable to conversion to low- and intermediate-energy gas. The amount of fuel consumed in a refinery is largely a function of (1) refinery size, which can vary from less than 5000 barrels of crude per day to over 400,000 barrels per day; and (2) refinery complexity, a function of the number and type of different processing operations.

GASIFIER CLEANUP SYSTEM CONSIDERATIONS

A variety of commercially available gasification systems were considered as possible candidates for each of the two model industries selected. Table 3 is a list of gasification processes which are commercially available. Several characteristics were taken into account in selecting gasification systems for each of the model plants. These considerations were:

(1) Unit size and turndown ratio of the gasifier. Unit size determines the number of units required for satisfying the energy demand of the industrial plant. Unit size of turndown ratio is combined to determine the flexibility of the system in meeting the varying load demands of the plant. For each model plant, a gasifier unit size was selected such that three to four gasifiers could satisfy the energy demand of the industrial plant. This number of units would supply adequate flexibility and yet not be so numerous as to cause undue plant complexity and high cost.

(2) The ability of the gasification system to gasify the coals that are available at the industrial plant was also considered an important aspect of the design. Nonagitator fixed-bed units, shown in table 3, are generally restricted to coals with free-swelling index less than 3. Agitator-type fixed-bed units are generally capable of handling slightly higher caking coals, up to a free-swelling index of about 7. Entrained slagging type processes are generally considered capable of handling any type of coal, although coals with a high grindability index and low moisture content are considered more attractive due to the necessity for pulverization. The one fluid-bed unit shown in table 3 would be restricted to mildly caking coals.

(3) Another important consideration is the byproducts produced in the gasification process. In the low-temperature processes, i.e., fixed-bed processes, these byproducts are generally tars, oils, phenols, and ammonia. Some steam could be produced by the waste heat from the gasifier, but this would not be considered a substantial product. Conversely, the high-temperature entrained slagging processes produce significant amounts of steam, but—due to their high temperature, produce little chemicals such as oils, tars, phenols, or ammonia. If a particular industry has a need or use for either the steam or chemical byproducts produced in the gasification process, then one type of process or the other may be considered more attractive.

A wide variety of gas desulfurization systems were also considered in the selection. These included physical sorbent systems which usually operate at pressures of about 300 psig, chemical absorption systems which usually operate at about atmospheric pressure, and

Table 3. Commercial gasifiers considered for model industry plants

Gasifier	Bed Type	Unit Output 10^9 Btu/day	Potential Byproducts	Limitations
Lurgi	fixed/agitator	8-12	tar, oil, phenols, NH_3	needs sized low-caking coal
Koppers-Totzek	entrained/slagging	8-10.5	steam	oxygen-blown only, pulverized coal
Wellman-Galusha	fixed/agitator	1.5-2.5	tar, oil, phenols, NH_3	needs sized low-caking coal
Applied Technology	fixed/2-stage	0.2-2.3	tar, oil, phenols, NH_3	needs sized coal, FSI <3
Winkler	fluidized	1.3-14	steam	needs crushed low-caking coal
Riley Morgan	fixed/agitator	1.8-3.0	tar, oil, phenols, NH_3	needs sized low-caking coal
Woodall Duckham	fixed/2-stage	1.0	tar, oil, phenols, NH_3	needs sized coal, FSI <3
Babcock & Wilcox	entrained/slagging	15	steam	primarily O_2-blown, pulverized coal
M.W. Kellogg	fixed/agitator	2.5-3.5	tar, oil, phenols, NH_3	needs sized low-caking coal
Wilputte	fixed/agitator	0.8	tar, oil, phenols, NH_3	needs sized low-caking coal

physical-chemical absorption systems which involve a combination of physical and chemical absorbents. Physical sorbent processes have a high absorptivity for sulfur in the gas, but also remove hydrocarbons. The removal of hydrocarbons from the fuel gas is undesirable. They also tend to remove carbon dioxide as well as sulfur compounds, thus complicating sulfur recovery. Chemical absorption processes are selective for hydrogen sulfide over carbon dioxide and have very low absorptivities for hydrocarbons. These processes, however, are not capable of removing sulfur to as low a concentration as physical sorbent processes. Physical-chemical absorption processes combine some of the positive features of both the physical and chemical type processes, but also involve some compromises. In the chemical absorption processes, sulfur can either be recovered from a hydrogen-sulfide rich gas stream resulting from the stripping of the sorbent solution or from direct oxidation of hydrogen sulfide to sulfur in the sorbent solution itself. After reviewing these systems, it was decided to select a clean-up system which is commonly recommended by the particular gasifier vendor of the selected gasification system, as this would be the most likely choice should a plant actually be constructed.

A final sulfur level in the fuel gas of 300 ppm was selected somewhat arbitrarily for both plants on the basis of several considerations.

(1) The limit would allow both plants to operate within the most stringent state SO_2 emissions standards for coal-fired processes.

(2) This low limit was judged adequate to limit corrosion in piping and possible sulfidation of products although more research is necessary to accurately define these limits.

(3) It represents a lower practical limit for atmospheric cleanup systems such as those studied. Both types of systems studied can achieve lower concentrations, but at higher cost and with the possibility of more complex sulfur recovery.

MODEL STEEL PLANT DESCRIPTION

The secondary steel plant selected as a model has a steel production capacity of 1,110,000 tons per year. The mill has production facilities for producing rolled bars, cut and coiled rod, and merchant products such as angles and channels. Some finished products such as wire and nails are also made in the model plant. The energy demand of this plant ranges from a minimum of 15 X 10^9 Btu/day to a maximum of 23 X 10^9 Btu/day with an average energy demand of 20 X 10^9 Btu/day. Minimum demand usually occurs on weekends and during down time for plant maintenance. Table 4 summarizes the characteristics of the steel plant model.

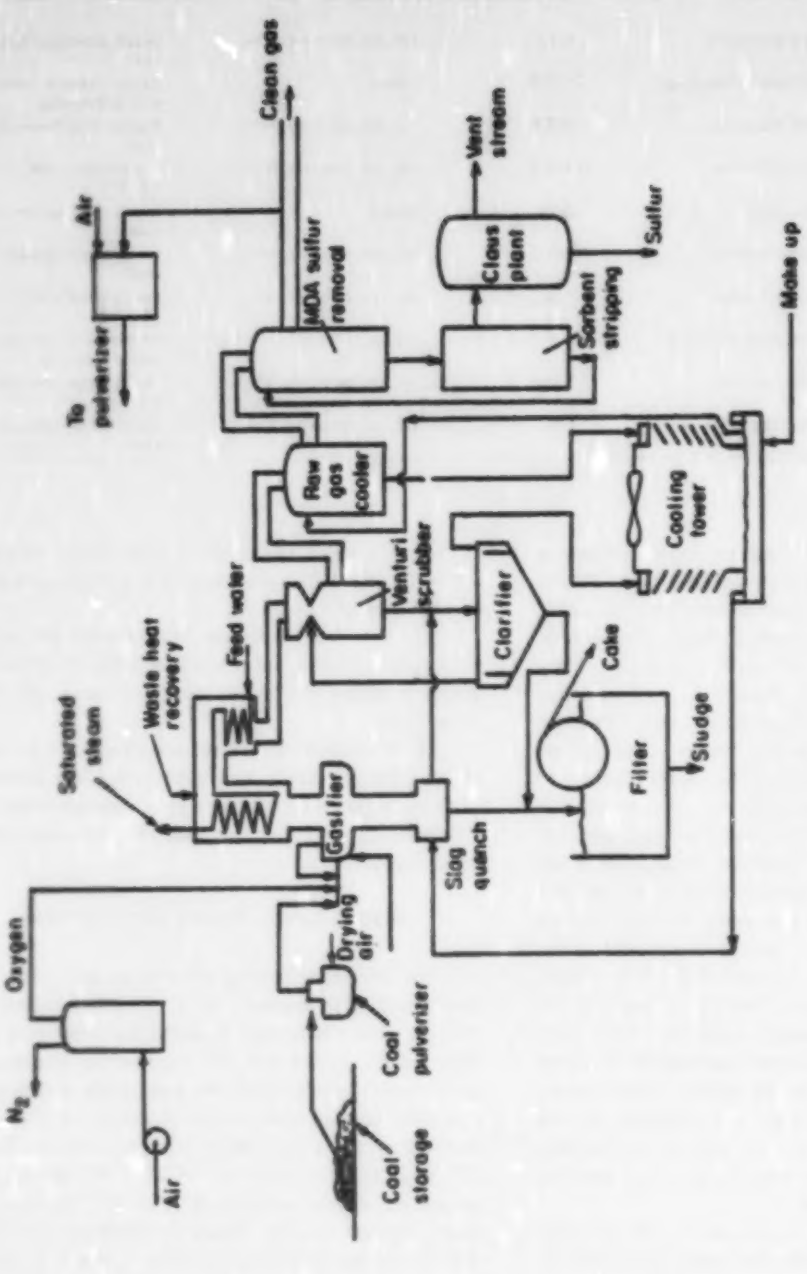

Air
N_2
Oxygen
Coal storage
Coal pulverizer
Drying air
Gasifier
Saturated steam
Waste heat recovery
Feed water
Slag quench
Venturi scrubber
Clarifier
Cake
Filter
Sludge
Raw gas cooler
Cooling tower
Make up
MDA sulfur removal
Sorbent stripping
Claus plant
Sulfur
Vent stream
Clean gas
To pulverizer
Air

Figure 3. Koppers Totzek/MDEA steel mill gasification plant.

Table 4. Steel plant statistics

Molten steel capacity	**ton/year** 1,110,000
Rolled bars	170,000
Cut and coiled rod	280,000
Angles, channels	360,000
Energy demand	**10^9 Btu/day**
Maximum	23 (peak production)
Average	20 (normal production)
Minimum	16 (weekends, downtime)

A Koppers-Totzek gasification system was selected for the steel plant model. This plant would consist of four two-headed gasifier units and would gasify about 1900 ton/day of coal producing approximately 22.3 X 10^9 Btu/day of fuel gas with a high-heating value of 286 Btu per standard cubic foot. An MDEA (methyldiethanolamine) cleanup system was selected for use in desulfurizing the fuel gas. This process, which operates at atmospheric pressure is commonly recommended by Koppers in such applications. Figure 3 shows an overall flow sheet of the gasifier and gas cleanup system.

The Koppers-Totzek process is restricted primarily to oxygen-steam gasification producing intermediate-energy gas of about 300 Btu per standard cubic foot. The intermediate-energy gas was considered desirable for the steel mill application after reviewing the combustion requirements of the various furnaces in the plant. Conversion of these processes to a gas with a lower heating value would require extensive conversion and modification.

The coal selected for the steel mill model was a lignitic coal with a moisture content of about 27 percent and a sulfur content of 1.7 percent. This coal would be pulverized to 70 percent through a 200-mesh screen and dried during the pulverization step to less than 4 percent surface moisture before feeding to the gasifier.

Gas produced in the gasification step would be passed through a waste-heat boiler for steam recovery and then through a two-stage venturi scrubber for removal of particulates and any tars that may be formed in the process. Because the Koppers-Totzek gasifier operates at such a high temperature (about 3300° F), only trace amounts of tars, phenols, oils, and a relatively small amount of ammonia are present in the fuel gas. From the venturi scrubber the gas would be processed through a cooler and then into the MDEA sulfur-removal system for removal of sulfur compounds.

The final fuel gas would contain about 300 ppm of sulfur compounds and the overall efficiency of the gasification process would be about 70 percent. Statistics on the gas plant design are summarized in table 5.

Figure 4 shows a representative plot plan of the steel mill with the gasifier and coal-storage piles included. The steel mill proper covers about 230 acres of land with approximately 70 acres of land in building area. Though the buildings in figure 4 are shown linked together, in reality they would be interspersed throughout the available area and relatively little free land would be available in the steel mill proper. The gasification and gas-cleaning plant is estimated to require about 15 acres of land and storage for a 1-month supply of coal would require additional 2-1/2 acres.

MODEL REFINERY DESCRIPTION

The model plant developed for representing the refinery industry would process about 25,000 barrel/day of crude oil. (See table 6.) Products produced at the refinery would consist primarily of residual oil, gasoline, and distillate oil. In the summer the refinery would convert a large percentage of residual oil to asphalt and in winter this residual oil would be sold as heating oil. The refinery processes a low-sulfur crude oil with less than 1 percent sulfur.

Total energy demand of the refinery is 7.2 X 10^9 Btu/day in the winter and 5.79 X 10^9 Btu/day in the summer. This demand could be satisfied by a mixture of refinery waste gas and low-energy gas from coal. The refinery gas contains a significant amount of propane, butane, and hydrogen—equivalent to about 0.67 X 10^9 Btu/day. For this study, these constituents are assumed to be 98 percent removed and sold. The remaining refinery waste gas consists primarily of methane, ethane, and some nitrogen and has a heating value of about 1,062 Btu per standard cubic foot. This gas would supply about 2.46 X 10^9 Btu/day of energy, and the remainder would have to be satisfied by a low-energy gas from coal.

Table 5. Gasification plant design for steel mill model

Gasifier - Koppers-Totzek
Desulfurization - MDEA (methyl diethanolamine)
Number of units - 4
Gas production rate - 22.3 x 10^9 Btu/day
Gas heat value - 286 Btu/scf
Coal consumption - 1900 ton/day
Efficiency - 70 percent

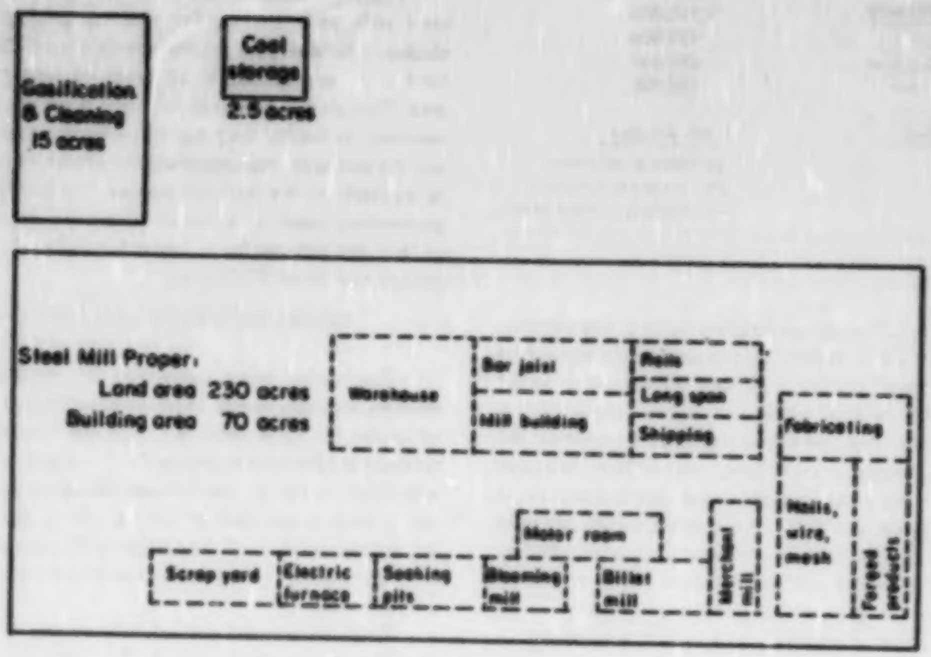

Gasification
& Cleaning
15 acres
Coal storage
2.5 acres
Steel Mill Proper:
Land area 230 acres
Building area 70 acres
Warehouse
Bar joist
Mill building
Rails
Long span
Shipping
Fabricating
Motor room
Scrap yard
Electric furnace
Soaking pits
Blooming mill
Billet mill
Merchant mill
Nails, wire, mesh
Forged products

Figure 4. Steel mill plot plan.

The coal selected for use in this system was an Eastern bituminous-type coal with 6 percent moisture, 8 percent ash, and sulfur content of 3.9 percent. The free-swelling index of this coal is about 5, dictating the use of an agitator-type fixed-bed gasifier.

Table 6. Refinery plant statistics

	Summer	Winter
Crude oil capacity 25,000 barrel/day		
Products (barrel/day)		
Residual oil	1600	4750
Gasoline	12,700	11,525
Distillate oil	9825	4600
Total Energy Demand (10⁹ Btu/day)	5.79	7.20
Refinery waste gas	2.46	2.46
Low-energy gas demand	3.33	4.74

Due to the low overall energy demand of the refinery, an air-blown fixed-bed, Wellman Galusha gasification system was selected for study. The gasification plant would supply about 4.74 × 10^9 Btu/day in the winter and 3.33 × 10^9 Btu/day in the summer. The mixture of refinery waste gas at 1,062 Btu per standard cubic foot and low-energy gas from the Wellman Galusha at 168 Btu per standard cubic foot would have a heating value of about 264 Btu per standard cubic foot in the winter and 234 Btu per standard cubic foot in the summer.

Figure 5 shows the flow sheet for the Wellman-Galusha gasification plant.

Due to the small size of the plant, it was not felt practical to install coal preparation facilities; therefore, crushed, sized coal would be purchased from the mine and stored at the gasification plant. The gas plant would consist of three 10-ft diameter Wellman-Galusha units capable of producing a total of 4.77 × 10^9 Btu/day of fuel gas with a heating value of 168 Btu per standard

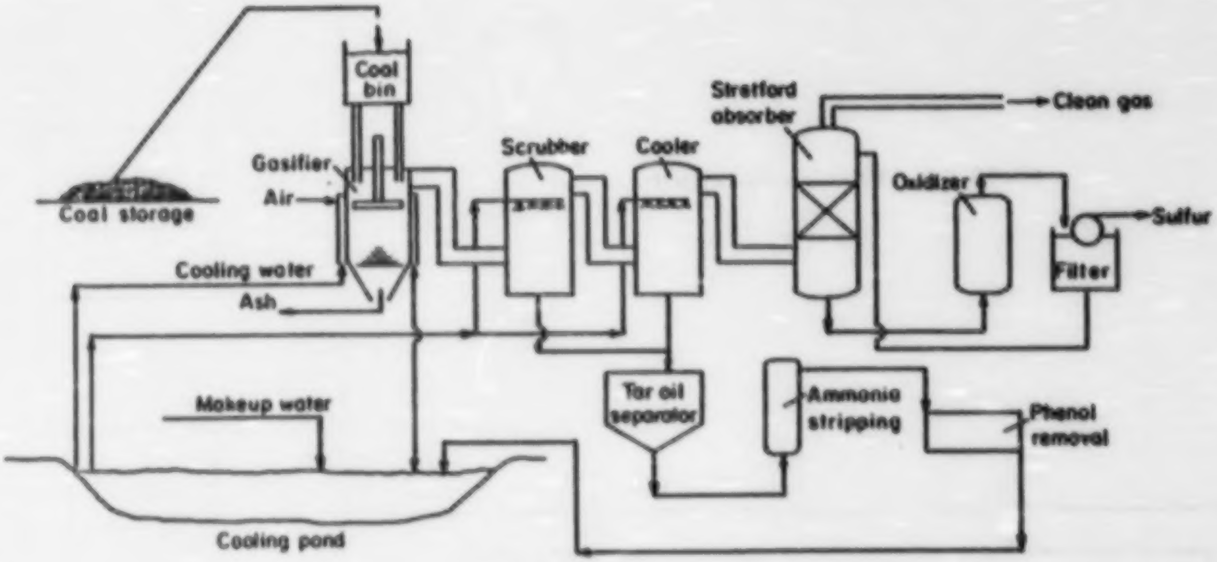

Coal bin
Gasifier
Air
Coal storage
Cooling water
Ash
Scrubber
Cooler
Stretford absorber
Clean gas
Oxidizer
Sulfur
Filter
Tar oil separator
Ammonia stripping
Phenol removal
Makeup water
Cooling pond

Figure 5. Flow sheet for the Wellman-Galusha gasification plant.

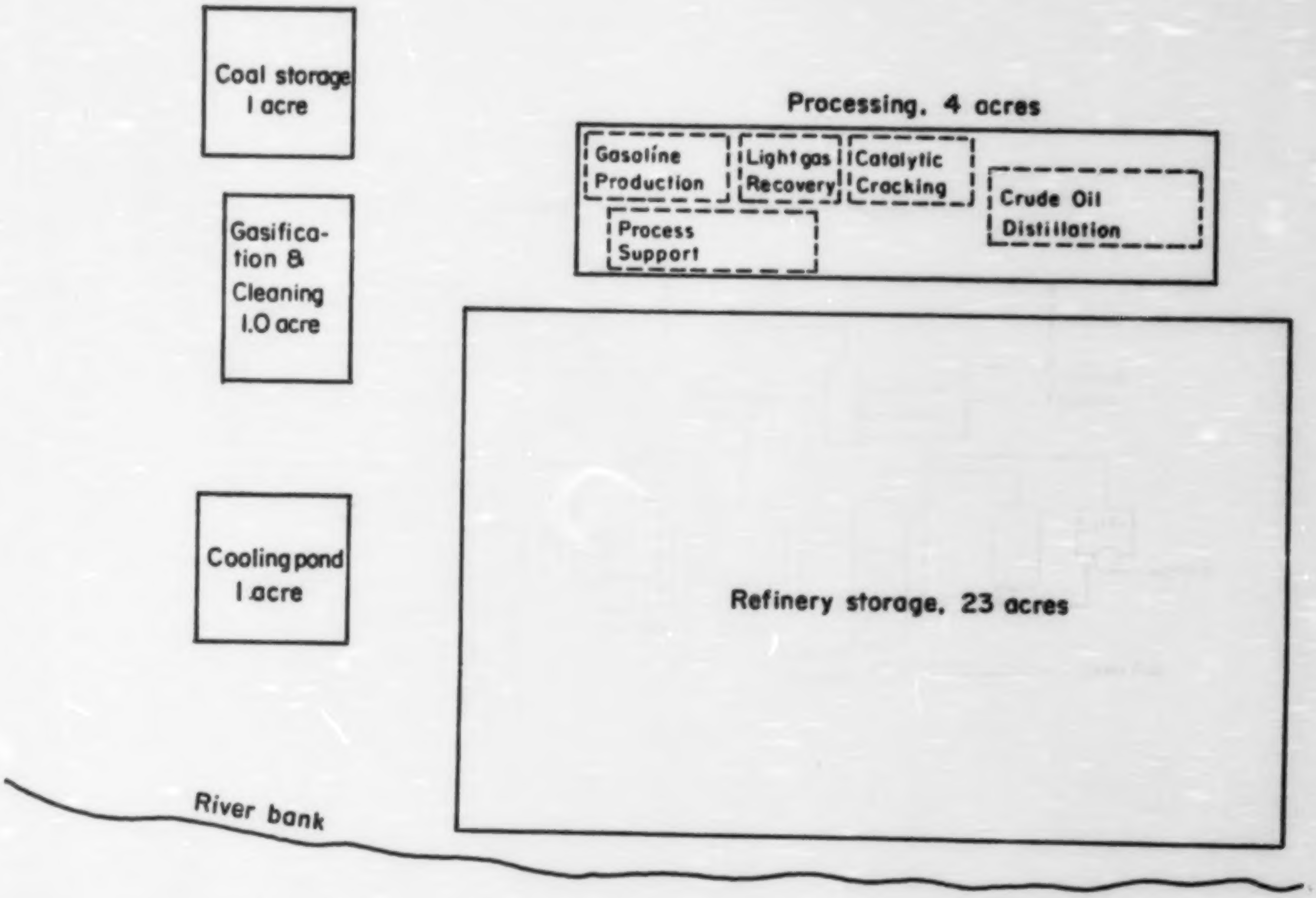

Coal storage
1 acre
Gasification & Cleaning
1.0 acre
Cooling pond
1 acre
Processing, 4 acres
Gasoline Production
Light gas Recovery
Catalytic Cracking
Crude Oil Distillation
Process Support
Refinery storage, 23 acres
River bank

Figure 6. Refinery plot plan.

cubic foot. The coal consumed would be about 252 ton/day and the overall thermal efficiency of the plant would be 78.7 percent. The raw gas from the gasifier is processed directly through a scrubber for the removal of tars, oil, phenols, and ammonia, and then through a cooler section where additional ammonia, tars, and other condensible constituents are removed. The gas is then fed into a Stretford-type desulfurization system which oxidizes sulfur compounds to elemental sulfur in solution, eliminating the need for a Claus plant. The final gas product would contain 300 ppm of sulfur, or less, and would be mixed with refinery gas and distributed to the various processes in the refinery. Table 7 summarizes the pertinent characteristics of the refinery gasification plant.

Table 7. Gasification plant design for refinery model

Gasifier - Wellman-Galusha (3 units)
Desulfurization - Stretford
Gas production rate - 4.77 x 10^9 Btu/day
Gas heat value - 168 Btu/scf
Coal consumption - 252 ton/day
Efficiency - 78.7 percent

Figure 6 shows an overall plot plan of the refinery with gasification and coal storage facilities and also the required cooling pond. The processing facilities of the refinery itself occupy about 4 acres of ground, and storage capacity requires an additional 23 acres of ground. The gasification plant for the refinery is estimated to require about 1 acre of ground with an additional 1 acre required for a cooling pond. Storage facilities for 1-month supply of coal would require an additional 1 acre.

EMISSIONS FROM THE GASIFICATION PROCESSES

Model Steel Plant

Table 8 summarizes the major emissions from the gasification process for the model steel plant. The major points of emissions in this process are the coal storage, coal pulverizing and preparation facilities, the oxygen plant, the filter which separates water from slag and clarifier sludge, cooling tower, and the Claus sulfur recovery process.

Emissions from the coal storage pile will involve fugitive dust picked up by the wind and leachate resulting from rain water filtering through the coal pile. The coal pile should be packed tight to limit dust loss and conveyors should be hooded with the hood exhaust processed through a baghouse or electrostatic precipitator. Leachate from the coal pile would resemble acid mine drainage in many respects—containing acids, organics, and soluble metals. This water should be collected and ponded for biological reduction of pollutants before being discharged to a water course. These problems can be minimized by coating the coal pile with a plastic material and drawing from it only during periods of emergency. The coal would normally then be taken directly from unit train or barge by covered conveyors.

Emissions from the coal pulverizing preparation step consists of pollutants in the gas used in drying the coal. A portion of the final product gas is combusted to heat air which is then supplied to the pulverizer for drying purposes. This stream is then vented from the pulverizer. The stream consists primarily of carbon dioxide, nitrogen, some water vapor, and oxygen. The stream would also contain particulates and possibly some small amounts of sulfur dioxide oxidized from the coal.

The vent stream from the coal preparation step should be processed through a baghouse or electrostatic precipitator or some other efficient particulate removal device for controlling particulate emissions. Emissions of other constituents would be relatively minor at this stage.

To limit dust loss, the entire coal pulverization facility should be located in a building with positive ventilation control. The exhaust from the building would then be processed through a particulate control device.

The discharge from the oxygen plant would involve primarily nitrogen which is not considered a harmful emission and would require no control.

The sludge from the filtration process which separates water from the slag and clarifier sludge is relatively inert and could be filled or ponded. As a result of the use of a filter, this sludge would have a low water content. The sludge would typically contain compounds common in coal ash and should require little or no treatment.

A significant discharge to the atmosphere would be the cooling tower plume. The cooling tower water would contain dissolved constituents from the scrubber circuit that overflows from the clarifier. These constituents would be present to some extent in the drift loss or plume from the cooling tower. Although many of these compounds may be present only in infinitesimal amounts when combined with the water in the plume,

Table 8. Discharges from steel mill model gasification plant

Source	Area of Impact	Amount	Composition	Percent
Coal storage - fugitive dust and leachate from rain	Air, Water	dependent on wind and rain conditions	coal dust acids organics soluble metals	
Coal pulverizing	Air	492, 160 lb/hr (or 112, 144 scfm)	CO_2	2
			N_2	68
			H_2O	13
			O_2	17
Oxygen plant	Air	72, 704 scfm	N_2	100
Filter	Water, Solid Waste	21, 616 lb/hr	C	17.8
			Ash	72.2
			H_2O	10.0
Cooling tower plume	Air	17,500 lb/hr	H_2O	100
Claus	Solid Waste (byproduct)	1,704 lb/hr	S	100
Claus tail gas	Air	675 scfm	H_2S	2.7
			CO_2	97.3

they may create a corrosion or health menace in the area around the plant. A solution to this problem is to use dry cooling towers or a cooling pond—either of which would involve much greater cooling area.

About 1704 lb/hr of elemental sulfur would be produced from the Claus plant in this process. This sulfur would be of marketable quality and could be stored and shipped. The Claus process, however, only removes about 95 percent of the sulfur compounds of the inlet stream. The resulting tail gas or vent stream from the Claus process, therefore, would contain hydrogen sulfide and CO_2. With the system shown this tail, gas could be blended with the product gas from the gasifier and combusted without exceeding even the strictest state limitations on sulfur dioxide emissions.

Model Refinery Plant

The major emissions from the refinery model gasification plant are shown in table 9. Sources of emissions are coal storage, the gasifier itself, scrubber effluent, and emissions from the Stretford desulfurization process.

Effluents from coal storage would involve similar considerations to those discussed for the steel plant model. Because crushed, sized coal would be purchased from the mine, however, dust loss for the refinery would be less than for the steel plant due to the lower percentage of fines or small particles.

About 1768 lb/hr of dry ash would be emitted from the gasifier in the form of bottom ash and could either be trucked or sluiced to a pond or landfill site. This ash should present no serious disposal problems.

The effluent from the scrubber system contains significant amounts of tars, ammonia, and phenols, which would have to be treated prior to disposal. In some cases these products may be able to be used in the industrial plants or marketed. For instance, in the case of the refinery, the recovered tars could possibly be used in the making of asphalt to supplement residual oil supplied. However, this would have to be evaluated as to the effect of these tars on the asphalt production process of the plant. Tars would be recovered by decantation and would result in a composition of about 91 percent tar, and 9 percent water. Ammonia and other compounds such as trace amounts of hydrogen sulfide which may be dissolved in the scrubber water, could be steam stripped and recovered for sale. Phenols could also be recovered for use through the so-called Phenolsolvan process, or they could be biologically reduced to sludge and separated from the water for disposal.

There is no immediate use for phenols in the refinery so biological reduction would probably be employed. The economics of this versus recovery of the phenols in a potentially more expensive process would have to be evaluated further.

Table 9. Discharges from refinery model gasification plant

Source	Area of Impact	Amount	Composition	Percent
Coal storage - fugitive dust and leachate from rain	Solid Waste	depends on wind and rain conditions	coal dust acids organics soluble metals	
Scrubber effluents	Water			
Tar separation		1153 lb/hr	tar H_2O	91 9
NH_3 stripping		1096 lb/hr	NH_3 H_2O	20 80
Phenols		120 lb/hr	phenols	100
Stretford	Solid Waste (byproduct)	777 lb/hr	sulfur	100

The Stretford desulfurization process for this particular design would produce about 770 lb/hr of elemental sulfur which would be stored and sold.

EMISSIONS FROM COMBUSTION PROCESSES

Emissions from combustion processes fall generally into four categories: (1) emissions of sulfur dioxide, (2) oxides of nitrogen, (3) particulates, and (4) trace constituents such as polycyclic organic matter or heavy metals.

In the gasification process, sulfur compounds in the coal are converted to sulfur compounds in the gas on almost a quantitative basis. The major sulfur-bearing constituent is hydrogen sulfide with minor amounts of carbon-sulfide (COS), carbon disulfide (CS_2), and mercaptans. If these compounds are not removed prior to combustion of the fuel gas, they are oxidized quantitatively to sulfur dioxide in the eventual flue gas from the combustion process. These expected emissions are shown in figure 7 as a function of coal sulfur and heat content. As can be seen from figure 7, a coal-sulfur content of from 0.5 to 0.8 percent would be required for most coals before compliance with the Federal standard of 1.2 pounds of SO_2 per million Btu heat input could be met. Coals for both the steel plant model and refinery plant model were assumed to contain over 1 percent sulfur, thus requiring some form of desulfurization. Figure 8 shows the expected emissions of sulfur dioxide from combustion processes as a function of sulfur content in the fuel gas for different fuel-gas heating values.

To meet the Federal standard for new sources of 1.2 pounds of SO_2 per million Btu heat input based on the gas heating value, a sulfur level in the fuel gas of only about 1000 ppm would be required even for low-energy gas. As the heating value of the gas rises, the allowable sulfur content also rises. Many states, however, have tighter standards for SO_2 emissions than the Federal standard, and it appears that the trend is for tighter standards to be promulgated. The New Mexico standard (.34 pounds of SO_2 per million Btu) would require a maximum of about 300 ppm sulfur in the gas to be

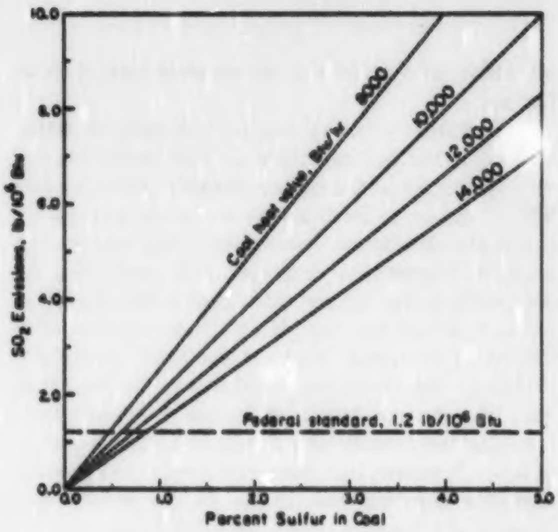


Figure 7. SO_2 emissions versus sulfur in coal.

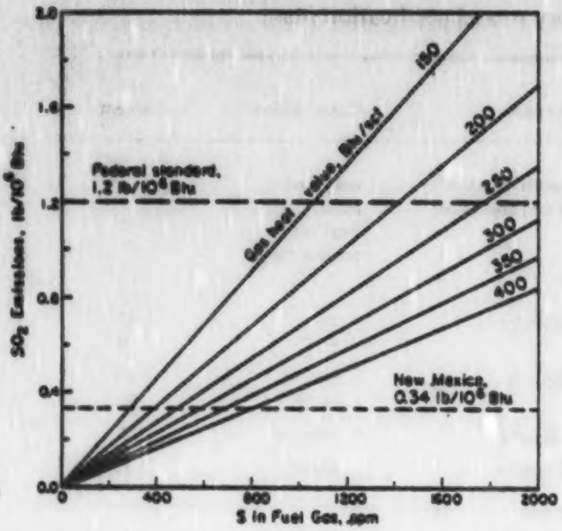


Figure 8. SO_2 emissions versus sulfur in fuel gas.

acceptable with a 150 Btu per standard cubic foot of fuel gas.

In addition to environmental limitations on sulfur content in the fuel gas, there are also certain process considerations in an industrial application. Hydrogen sulfide is known to have a high corrosion potential in piping and distribution systems, especially when in the presence of water vapor or oxygen. Also, when firing the gas directly in the furnace, sulfur compounds in the fuel gas such as hydrogen sulfide can cause problems with sulfidation of certain kinds of products, particularly high-grade steel products. Determining the maximum limit of sulfur compounds in the gas to prevent these problems from occurring will require further research. However, it appears that these requirements will be more restrictive than the new source Federal performance standard of 1.2 pounds of SO_2 per million Btu.

For this study, a maximum sulfur concentration in the fuel gas of 300 ppm was established. Besides being an acceptably low value of sulfur concentration in the gas for most all environmental purposes, this value was also felt to be sufficiently low to limit the adverse effects of sulfidation and corrosion of piping. This value is also a reasonable lower bound on what can easily be achieved by atmospheric pressure, chemical-absorption type sulfur removal systems without unusually high operating costs, or complex sulfur recovery processes.

Formation of oxides of nitrogen in combustion processes is primarily the result of two mechanisms: fixation of airborne nitrogen in the combustion air, and oxidation of fuel-bound nitrogen. The thermal fixation of nitrogen carried in with the combustion air is primarily a function of available oxygen in the flue gas products and combustion temperature. Oxidation of fuel-bound nitrogen—primarily ammonia and HCN for low- and intermediate-energy gas, is mostly a function of the content of nitrogen in the fuel gas and the availability of oxygen (or the stoichiometry) of the resulting combustion products. Temperature in this case is of little importance.

In comparing thermally produced NO_x from natural flames and flames with low- or intermediate-energy gas, the primary consideration would be adiabatic flame temperature if constant firing rate and stoichiometry or percent excess air is assumed. The resulting thermal NO_x produced would then have to be adjusted for the amount of diluent (nitrogen) entering with the combustion air in both cases. Table 10 shows representative adiabatic flame temperatures for natural gas and the gases produced for the steel mill and refinery plant models. As can be seen, the Koppers-Totzek gas is slightly higher than natural gas in flame temperature, and the mixture of refinery gas and Wellman-Galusha gas is slightly lower. Because less air is required for natural gas, a lesser amount of nitrogen is available for fixation; thus, the amount of thermal NO_x formed must be adjusted for this amount. The expectant relative thermal NO_x production of natural gas and the substitute fuels for the two model plants is shown in table 11. As can be seen, in both the refinery and steel plant model cases a reduction would be expected in the production of thermal NO_x.

Oxidation of fuel-bound nitrogen, however, involves different considerations. Because natural gas contains essentially no ammonia, any nitrogen in the low- or intermediate-energy fuel gas would result in an increase in NO_x emissions produced from fuel-bound nitrogen.

Table 10. Adiabatic flame temperatures of fuel gases[a]

Gas	High Heating Value, Btu/scf	Flame Temperature, F
Natural Gas	973	3500
Koppers-Totzek (steel mill)	286	3700
Wellman-Galusha (refinery mixture)	264	3200

---

[a] Theoretical adiabatic flame temperature including dissociation.

Table 11. Relative NO_x production of various fuels at 10 percent excess air

Fuel	Relative NO_x Production
Natural Gas	1.00
Koppers-Totzek (steel mill)	0.93
Wellman-Galusha (refinery)	0.74

Data on oxidation of fuel-bound nitrogen to NO_x, however, shows that the fuel-bound nitrogen is not quantitatively converted to NO_x, instead part of it is converted to elemental nitrogen which would not be considered a pollutant. It appears that the conversion rate of fuel-bound nitrogen to NO_x in the combustion products decreases as the concentration of fuel-bound nitrogen increases. It also appears that the conversion rate is relatively independent of the form in which the fuel-bound nitrogen exists in the gas. Figure 9 shows the results of a compilation of data from various sources on conversion of nitrogen in the fuel to NO_x in the combustion products. This curve shows that for low concentrations of nitrogen in the fuel gas, conversion of fuel-bound nitrogen to NO_x is essentially 100 percent and the conversion decreases to a minimum of about 15 percent at high concentrations of nitrogen.

Data on fuel-bound nitrogen content or ammonia content in fuel gas from coal is lacking. Table 12 gives some values of NH_3 concentrations obtained from the literature for four gasification processes. These processes include entrained slagging and fixed-bed operation using both air and oxygen as the gasifying medium. Table 12 also shows the expected NO_x emissions as a function of gas-heat value using the curve of Dykema-Hall from figure 9 for nitrogen conversion. The values shown in table 12 do not include thermally produced NO_x but, in some cases, they still exceed the Federal standard of 0.7 lb NO/10^6 Btu for solid fuel-fired systems and in all cases exceed the Federal standard of 0.2 lb NO/10^6 Btu for gas-fired systems. As stated above, these values are for the raw gas from the gasifier and in cleanup systems where water scrubbing is used (such as the two model plants), nearly all the ammonia in the fuel gas can be removed prior to combustion.

Particulate content in the final clean product gas from both of the gasification plant models in negligible. Combustion of this gas, therefore, would be expected to result in negligible particulate emissions to the atmosphere and no particulate control would be required. In both model plant cases, the low-energy gas would be replacing the firing of some heavy oil which would result in an overall decrease in particulate emissions from these two industries.

Emissions of trace organic constituents such as polycyclic organic matter (POM) are a function of the number of long chain hydrocarbons or ring-type hydrocarbons in the fuel itself and of the combustion conditions. Coal and oil both contain significant numbers of these compounds. However, the product gas from gasification should contain few, if any, long chain hydrocarbon components or ring-type hydrocarbon components. Combustion conditions for firing the fuel gas would be similar to those for firing natural gas; thus,

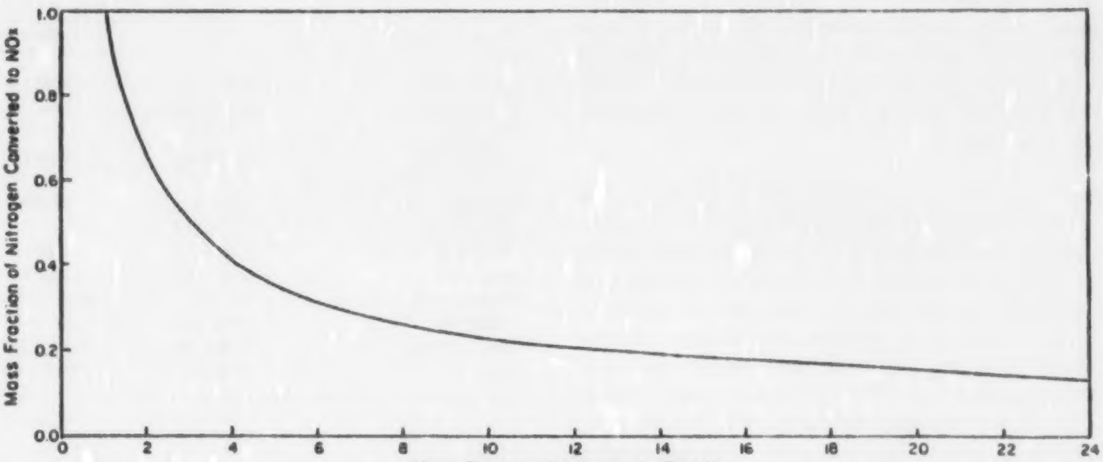


Figure 9. Fuel nitrogen converted to NO_x (ref. 5).

Table 12. Ammonia in raw gas

Process	NH_3 Volume Percent	NO_x lb/10^6 Btu[a]
Koppers-Totzek (O_2) (ref. 6)	0.17	0.44
2-Stage Entrained (air) (ref. 7)	0.38	1.46
Lurgi (pressurized O_2) (ref. 8)	0.70	0.83
Fixed Bed (atmospheric air) (ref. 7)	0.28	1.18

[a] Using relationship of figure 9.

emissions of these types of materials would be expected to be similar to that of natural gas. They would be significantly less than if the coal were fired directly or if oil were used directly as the fuel.

Other trace constituents, such as trace metals that may be vaporized in the combustion process, are also potential pollutants. The more volatile metals (mercury, etc.,), would be vaporized in the gasification process but subsequently condensed in the coal-gas cleaning process. Table 13 shows representative concentrations of trace elements in tar and condensate from the synthane reactor; thus emissions of trace elements would primarily be confined to the liquid and solid residue from the gasifier rather than to the combustion products.

Table 14 summarizes emissions from the two industrial plant models. These emissions would be compared with those from the industrial plant prior to conversion to gasification. The most notable increase in emissions from the combustion process is SO_2 emissions. In both cases, these emissions would be below the new-source Federal standard for SO_2 emissions for coal-fired sources. In the case of the steel plant model, it is assumed that the tail gas from the Claus plant is combined with the clean gas from the gasification plant. This approximately doubles the sulfur emissions from this particular process.

Other Aspects of Converting Industry to Gas From Coal

Most industrial furnaces can be converted to at least an intermediate-energy gas, without extensive modification. Many furnaces could also successfully be converted to low-energy gas, although the lower flame temperatures and larger flue gas volumes impose certain limitations on the type of furnace that could be successfully converted without extensive modification. In some cases, existing burners could probably be successfully modified for intermediate energy gas, especially if the gas heating value could be increased to about 400 Btu per standard cubic foot by removal of CO_2. However, in many cases, new burners would be required. For low-energy gas, new burners would almost always be required.

Most industrial natural gas distribution systems are designed for up to 125 to 150 pounds per square inch gage. However, natural gas is seldom distributed at this pressure and in many cases is distributed at 50 pounds per square inch gage or less. The distribution pressure is then normally reduced at the burner to pressures on the order of a few ounces per square inch gage. Under these conditions it may be possible to substitute at least an intermediate-energy gas in an existing natural gas distribution system although pressurization of the gas would be required.

Table 13. Trace elements in tars and condensate from Synthane - 40 atm PDU gasifier (ref. 9)

Constituent	Concentration (ppm) µg/g	
	Tar	Condensate
Arsenic (As)	0.71-1.6	0.001
Bismuth (Bi)	0.17-0.30	...
Boron (B)	12-17	43-82
Bromine (Br)	0.01-0.08	0.001
Cadmium (Cd)	0.16	...
Fluorine (F)	0.97-12	32-39
Gallium (Ga)	0.02-0.17	...
Germanium (Ge)	0.02-0.08	0.001
Lead (Pb)	0.16-0.48	0.003
Mercury (Hg)	0.21-1.2	0.027-0.030
Nickel (Ni)	0.95-1.6	0.001-0.018
Selenium (Se)	0.08-0.24	0.14-0.18
Zinc	0.48-3.3	0.007-0.13

Table 14. Effect on emissions from combustion sources

Particulate Emissions	Reduced – Particulate content of gas is negligible. Gas would replace some current oil- and coal-firing
SO_x	Increased – Steel Mill – 0.383 lb $SO_x/10^6$ Btu of gas 0.267 lb $SO_x/10^6$ Btu og coal Refinery – 0.200 lb $SO_x/10^6$ Btu of gas 0.232 lb $SO_x/10^6$ Btu of coal
NO_x Emissions	Reduced – Fuel gas contains negligible nitrogen (NH_3, HCN) and thermal NO_x would be less due to lower nitrogen content of flue gas.

CONCLUSIONS

Retrofitting industrial plants to low- or intermediate-energy gas presents many environmental considerations, but there appears to be little reason why such a retrofit cannot be done in an environmentally acceptable manner.

Sulfur and nitrogen compounds in the fuel gas (primarily H_2S and NH_3) represent the primary sources of atmospheric emissions from combustion processes. These constituents are also potentially corrosive, especially if any water vapor is present. Although the corrosivity of these constituents has not been accurately defined, it appears that their concentration in the fuel gas should be reduced below that which would be considered environmentally acceptable to minimize corrosion in the intricate and extensive gas distribution systems found in most industrial plants.

The major environmental hazard involves the gasification plant itself. The potential atmospheric emissions in the fuel gas become potential liquid and solid effluents. A variety of processes will be required for treating the various liquid streams used in cleaning and cooling the fuel gas. In many industries, water treatment systems are already in use similar to those that would be required for a gasification plant. In the refinery industry, for example, water treatment processes are commonly used for removing oils, phenols, ammonia, and H_2S; however, in almost all cases these treatment systems would have to be enlarged or additional processes added if a gasification plant were installed. The expertise and technology for treating these various streams in an environmentally acceptable manner are available.

The major factor in determining whether an industry would convert to low- or intermediate-energy gas is economics. Even a small gasification plant would involve many processes, most of which involve either cleaning the gas or treating various effluent streams associated with gas cleaning. These various cleaning systems also constitute the major cost in a coal gasification plant. Modifications required in furnaces are primarily determined by the heating value of the gas with higher heating value gases requiring fewer modifications. The requirement for complex gasification plants and attractiveness of a high grade fuel gas (such as intermediate-energy gas from an oxygen-blown gasifier) tend to favor large-scale industrial applications. Thus, gasification is most attractive for large, individual, industrial plants or groups of smaller plants in an industrial park.

REFERENCES

1. "A National Plan for Energy Research, Development, and Demonstration: Creating Energy Choices for the Future, Volume I: The Plan," Energy Research and Development Administration, ERDA-48, June 1975.
2. "1972 Census of Manufacturers," U.S. Department of Interior.
3. "Special Survey on Gross and Net Consumption of Fuels and Energy in the Iron and Steel Industry," American Iron and Steel Institute, May 1974.
4. *Oil and Gas Journal*, April 7, 1975.
5. Dykema, O. W., and Hall, R. A., "Analysis of Gas, Oil, and Coal Fired Utility Boiler Test Data," U.S. EPA Symposium on Stationary Source Combustion, September 1975.
6. Farnsworth et al., "Clean Environment With the Koppers-Totzek Process," EPA Meeting, Environmental Aspects of Fuel Conversion Technology, May 1974.

7. Robson, F. L., Giramonti, A. J., "The Environmental Impact of Coal Based Advanced Power Generating Systems," Symposium Proceedings, Environmental Aspects of Fuel Conversion Technology, pp. 237-257, October 1974, EPA 650/2-74-118.

8. Shaw, H., and Magee, E. M., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification, Section 1, Lurgi Process," July 1974, EPA 650/2-74-009C.

9. Forney, A. J., et al., "Trace Element and Major Component Balances Around the Synthane PDU Gasifier," August 1975, PERC/TPR-75/1.

COMBINED-CYCLE POWER SYSTEMS

F. L. Robson, W. A. Blecher, and A. J. Giramonti*

Abstract

The performance, cost, and emissions of integrated fuel processing/combined-cycle power systems are identified and compared to those of a coal-fired steam station.

Of the many types of advanced power systems being proposed as partial solutions to this country's long range energy problem, the COmbined Gas And Steam (COGAS) system is the only one currently in the commercial stage, with several thousand Mw already installed in utility systems. The systems now installed and those more advanced versions being proposed require a very clean fuel in order to assure reasonable gas turbine performance and lifetime. While these clean fuels can be produced from coal, the processes are inefficient, typically losing 20-30 percent of the original coal heating value. By integrating the fuel processing system with the COGAS power system, much of the inefficiencies which appear as process heat can be recovered, resulting in overall plants having efficiencies, costs, and emissions which are more attractive than present-day conventional coal-fired steam stations.

INTRODUCTION

The United States has been blessed with an abundance of coal, much of it in close proximity to large urban areas. This coal was used widely by the electric utilities to fuel their boilers. However, the advent of inexpensive imported oil displaced coal from many urban locations on the eastern seaboard, while many southern and western power stations switched to even cheaper natural gas. The use of coal has been further reduced by stringent sulfur emission regulations in many of the coal-producing States. By mid-1973, less than 55 percent of the power in the United States was generated from coal.

Research on methods of converting coal to a more environmentally acceptable fuel has been underway for a number of years. Additional impetus was given to these efforts by the OPEC-imposed oil embargo after the October War of 1973. Most of the coal conversion methods under investigation involve changing the coal to a new form, usually liquid or gas. This requires a considerable amount of energy, thus, it is typical that only 75 percent or less of the coal heating value is available as chemical energy in the resulting fuel. In order to be utilized economically in the utility industry, some method of more efficient electrical generation is required to overcome all or at least a major portion of this fuel cycle inefficiency.

One such system, identified some years ago (e.g., ref. 1,2), is the *COmbined Gas And Steam* or COGAS power system. More recently, the COGAS system has again been identified as the most attractive advanced power system (see figure 1 taken from ref. 3).

COMBINED-CYCLE POWER SYSTEM

There are a number of cycle configurations possible with COGAS or combined-cycle power systems. The steam boiler may be fired with additional fuel or it may be pressurized (supercharged) and serve as the combustor for the gas turbine. For applications using advanced, high-temperature gas turbines, the simple waste-heat recovery cycle shown schematically in figure 2 is the most attractive. Currently, several thousand Mw's of combined-cycle systems of this configuration are installed or on order for use with clean liquid fuels.

The major reasons for the current interest in COGAS systems are the high performance and low capital cost. These systems typically cost only 50-60 percent of a conventional steam power plant and have installation times of only 24-32 months. The performance on a clean liquid fuel such as home heating oil or jet fuel is currently around 41 percent with potential increases to 50 percent or more as gas turbine technology advances (figure 3).

COAL GASIFICATION

The gasification of coal has been carried out for commercial purposes for quite a long time. One of the first instances in this country was the use of gasified coal to produce illuminating gas for the Baltimore Gas Light Company in 1817. Prior to the widespread availability of inexpensive natural gas, much of this country's industry used atmospheric pressure gasifiers to provide fuel for metallurgical use, glassmaking, bakeries, etc.

For use in power generation with gas turbines, it is necessary to provide the fuel at pressures of 10 atmospheres or above. The only commercially available gasifier operating at pressure with coal is the fixed-bed type such as that offered by Lurgi. This system has several drawbacks, not the least of which is its high cost. There are

---

*The authors are with the United Technologies Research Center, East Hartford, Connecticut.

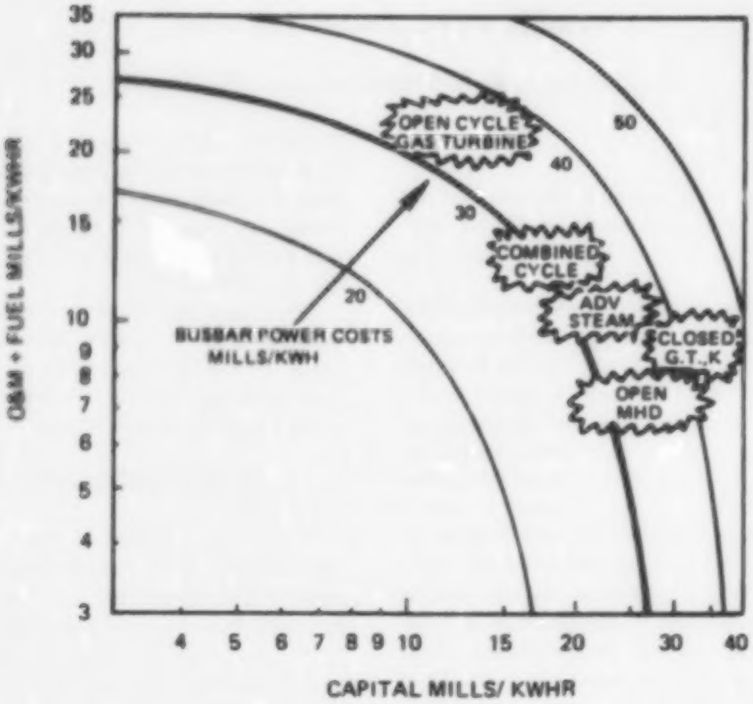


Figure 1. Preliminary ECAS results.

several more advanced pressurized gasifiers in various stages of development. These have the potential for more efficient and less costly production of fuel gas than does the fixed-bed gasifier. As part of a program on advanced COGAS systems carried out by UTRC under EPA Contract 68-02-1099, evaluations were made of several types of gasifiers including the Bureau of Mines fixed-bed gasifier and the Bituminous Coal Research (BCR) two-stage entrained flow gasifier. Because of the potential attractiveness, the BCR will be emphasized here.

A schematic of this gasifier with pertinent flows is shown in figure 4. A comparison of the off gases from this gasifier and the Bureau of Mines gasifier is given in table 1. As can be seen in table 1, both fuel gases contain quantities of H_2S, COS, and NH_3 which must be removed before combustion if environmental regulations are to be met.

GAS CLEANUP SYSTEMS

The fuel gas coming from the gasifier must be cleaned not only to meet the environmental regulations, but also to meet restrictions set by the gas turbine. The latter are often more stringent than those for the environment as can be seen in table 2. Here it is seen that particulates must also be removed.

Today, there is a large number of commercially available cleanup systems as has been pointed out by prior speakers (ref. 4). These systems operate at temperatures of 420 K or less, well below gasifier outlet temperatures. A simple schematic of a typical low-temperature cleanup system is shown in figure 5. Several of these systems have nearly equivalent performance. Consequently, a representative physical absorption system, the Selexol process of Allied Chemical Corporation, was selected for further consideration.

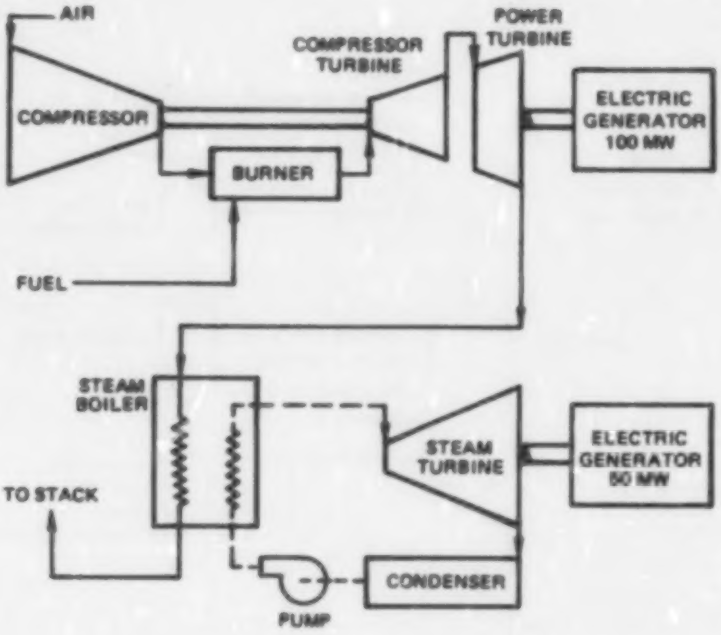

AIR
COMPRESSOR
COMPRESSOR TURBINE
POWER TURBINE
ELECTRIC GENERATOR 100 MW
BURNER
FUEL
STEAM BOILER
TO STACK
STEAM TURBINE
ELECTRIC GENERATOR 50 MW
PUMP
CONDENSER

Figure 2. Waste-heat COGAS system.

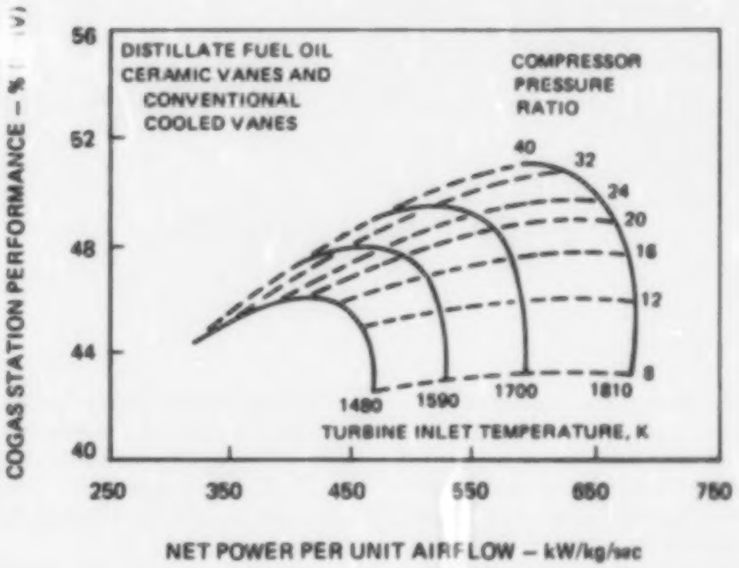


Figure 3. COGAS station performance.

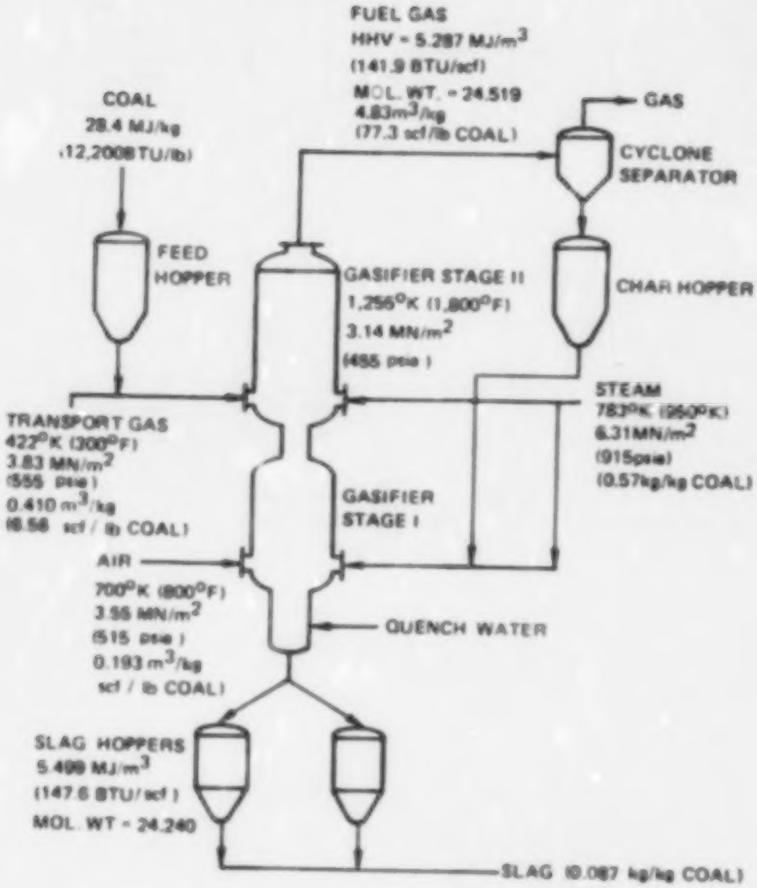

FUEL GAS
HHV = 5.287 MJ/m3
(141.9 BTU/scf)
MOL. WT. = 24.519
4.83m3/kg
(77.3 scf/lb COAL)
GAS
COAL
28.4 MJ/kg
(12,200BTU/lb)
CYCLONE SEPARATOR
FEED HOPPER
GASIFIER STAGE II
1,256°K (1,800°F)
3.14 MN/m2
(455 psia)
CHAR HOPPER
STEAM
783°K (950°K)
6.31MN/m2
(915psia)
(0.57kg/kg COAL)
TRANSPORT GAS
422°K (300°F)
3.83 MN/m2
(555 psia)
0.410 m3/kg
(6.56 scf / lb COAL)
GASIFIER STAGE I
AIR
700°K (800°F)
3.55 MN/m2
(515 psia)
0.193 m3/kg
scf / lb COAL)
QUENCH WATER
SLAG HOPPERS
5.499 MJ/m3
(147.6 BTU/scf)
MOL. WT = 24.240
SLAG (0.087 kg/kg COAL)

Figure 4. BCR entrained flow gasifier.

The use of the low-temperature cleanup system, while meeting all turbine and environmental restrictions, results in some degradation of performance because of the cooling of the fuel gas. By cleaning the gas at higher temperatures, at or near gasifier outlet for example, much of the sensible heat can be utilized in the cycle at maximum efficiency. Unfortunately, there are presently no high-temperature sulfur removal systems in more than simple bench-scale or rudimentary demonstration stages. One of the potentially more attractive methods of high-temperature cleanup involves the use of half-calcined dolomite as a sulfur remover. Considerable work on this process has been done by the Consolidated Coal Company, a part of the Continental Oil Corporation, and the CONOCO Process has been selected for presentation here.

It should be noted that in addition to sulfur removal, the low-temperature systems will also remove nearly all the soluble nitrogen compounds such as ammonia, cyanide, pyridine, etc. This necessitates an

Table 1. Fuel gas characteristics

Gasifier Type	Fixed-Bed*		Two-Stage Entrained-Flow	
Temperature, K (F)	811	(1000)	1255	(1800)
Pressure, MN/m^2 (psia)	3.45	(500)	3.45	(500)
Volume %				
N_2		47.61		47.70
CO		20.55		16.74
CO_2		5.88		8.84
H_2		13.83		11.98
CH_4		2.76		3.14
H_2S		0.60		0.46
COS		0.10		0.10
NH_3		0.25		0.38
H_2O		8.42		10.46
		100.00		100.00
Tar, kg/kg Coal		0.11		0.0
HHV, MJ/m^3 (Btu scf) [Tar Free]	5.212	(139)	4.687	(125)
Sensible Heat/Coal HHV, %	12.2		24.6	

*No tar recycle.

Table 2. Fuel gas cleanup requirements

	Low-Btu Gas	Typical Current Spec
Sulfur	0.05 Mol % or Less Than Amount to Form 0.6 ppm Alkali Metal Sulfate	<1.0 Mol % or Less Than Amount to Form 5 ppm Alkali Metal Sulfate
Particulates	4 ppm Weight or 0.0012 gr/ft^3 > 2 μ	30 ppm or 0.01 gr/ft^3
Metals		
Vanadium	< 0.003 ppm Weight	< 0.02 ppm Weight
	See Sulfur Spec	< 0.6 ppm
Nitrogen	500 ppm as NH_3	

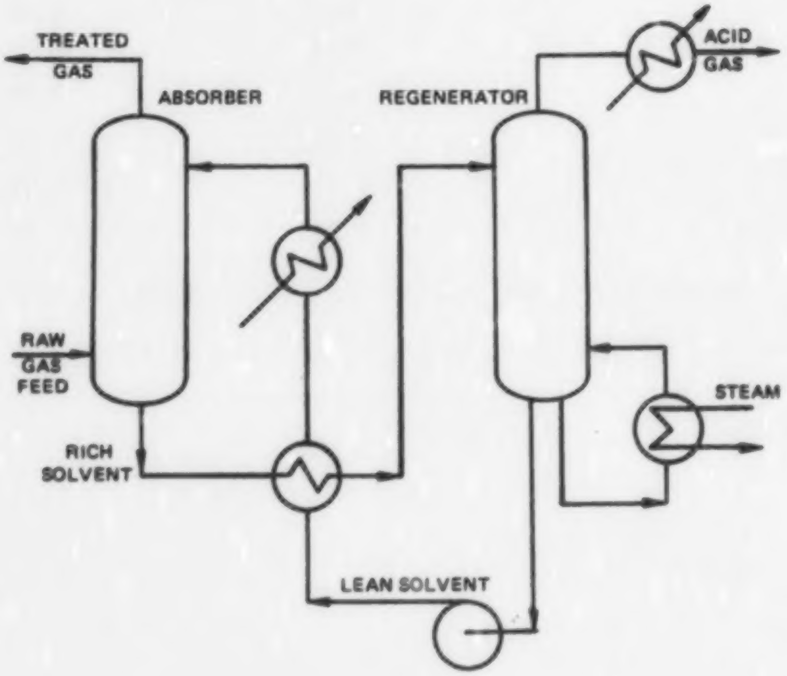

TREATED
GAS
ABSORBER
REGENERATOR
ACID
GAS
RAW
GAS
FEED
RICH
SOLVENT
STEAM
LEAN SOLVENT

Figure 5. Typical low-temperature acid gas removal unit.

ammonia removal system with additional utility loads. The high-temperature systems do not remove ammonia, or at least have not been documented to be capable of reviewing ammonia or other nitrogen compounds. Thus, an appreciable amount of fuel-bound nitrogen would be contained in the power system fuel.

INTEGRATED POWER SYSTEMS

To ensure that the highest performance results from coupling the coal processing and power systems, a very careful integration of components must be carried out. These are gasifier requirements for high-pressure air and steam which can be supplied from the power system; similarly, some of the cooling of the fuel gas prior to low-temperature cleanup could supply heat for use in the power system. Somewhat simplified schematics of the integrated systems based upon the BCR-type gasifier with low- and high-temperature cleanup are shown in figures 6 and 7.

The performance of the integrated systems is very much a function of gasifier type and turbine operating characteristics. For systems based upon fixed-bed gasifiers, a turbine inlet temperature of 1477 K (2200 F) was selected. Such an integrated system could be available in the late-1970 decade. Performance for this first-generation system with both low- and high-temperature cleanup is shown in figure 8 where it is compared to the performance of the distillate-fired COGAS system. The performance penalty associated with the low-temperature system is due to both thermodynamic penalty associated with cooling the gas and also to the relatively high utility loads of the cleanup system. The high-temperature cleanup process used in this system is based

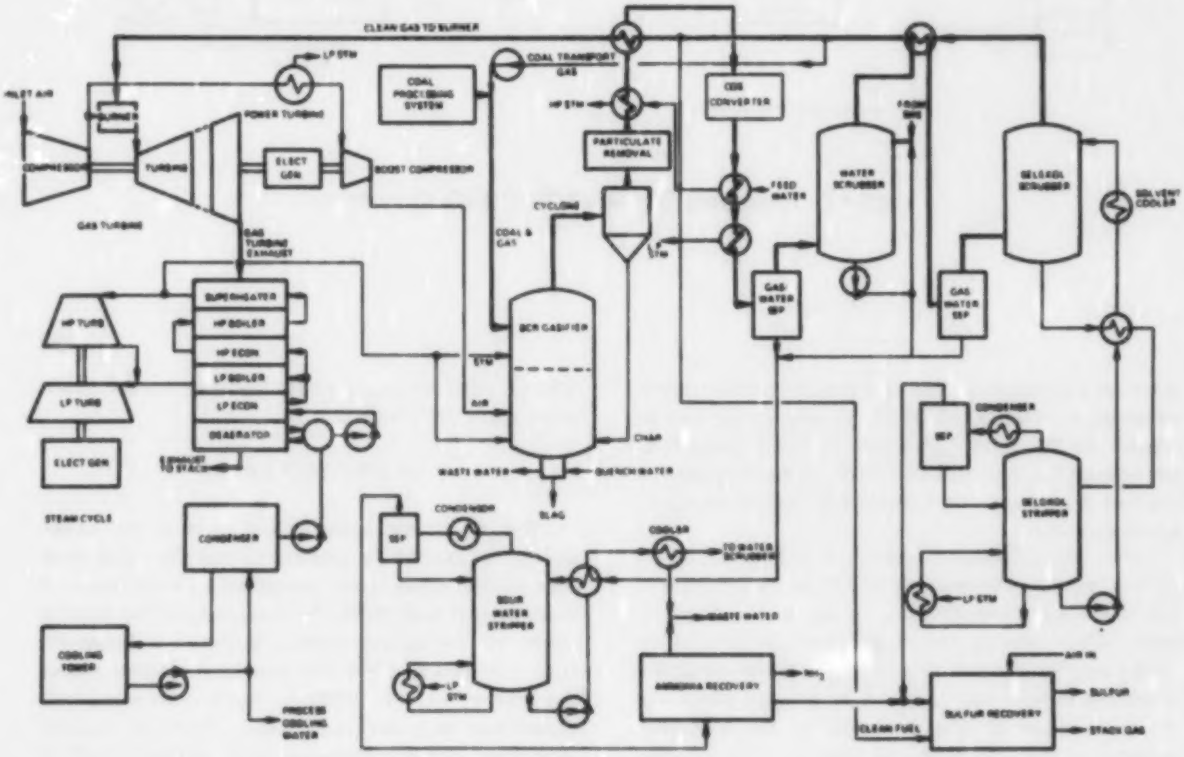

CLEAN GAS TO BURNER
LP STM
COAL TRANSPORT GAS
COAL PROCESSING SYSTEM
INLET AIR
BURNER
POWER TURBINE
COMPRESSOR
TURBINE
ELECT GEN
BOOST COMPRESSOR
GAS TURBINE
HP STM
PARTICULATE REMOVAL
CYCLONE
COAL & GAS
GAS TURBINE EXHAUST
SUPERHEATER
HP BOILER
HP ECON
LP BOILER
LP ECON
DEAERATOR
HP TURB
LP TURB
ELECT GEN
EXHAUST TO STACK
STEAM CYCLE
BCR GASIFIER
STM
AIR
CHAR
WASTE WATER
QUENCH WATER
SLAG
COS CONVERTER
FEED WATER
LP STM
GAS-WATER SEP
WATER SCRUBBER
FROM SWS
GAS WATER SEP
SELEXOL SCRUBBER
SOLVENT COOLER
CONDENSER
SEP
SELEXOL STRIPPER
LP STM
CONDENSER
COOLING TOWER
PROCESS COOLING WATER
SEP
CONDENSER
SOUR WATER STRIPPER
LP STM
COOLER
TO WATER SCRUBBER
WASTE WATER
AMMONIA RECOVERY
NH3
AIR IN
SULFUR RECOVERY
SULFUR
STACK GAS
CLEAN FUEL

Figure 6. Integrated COGAS/BCR/selexol system.

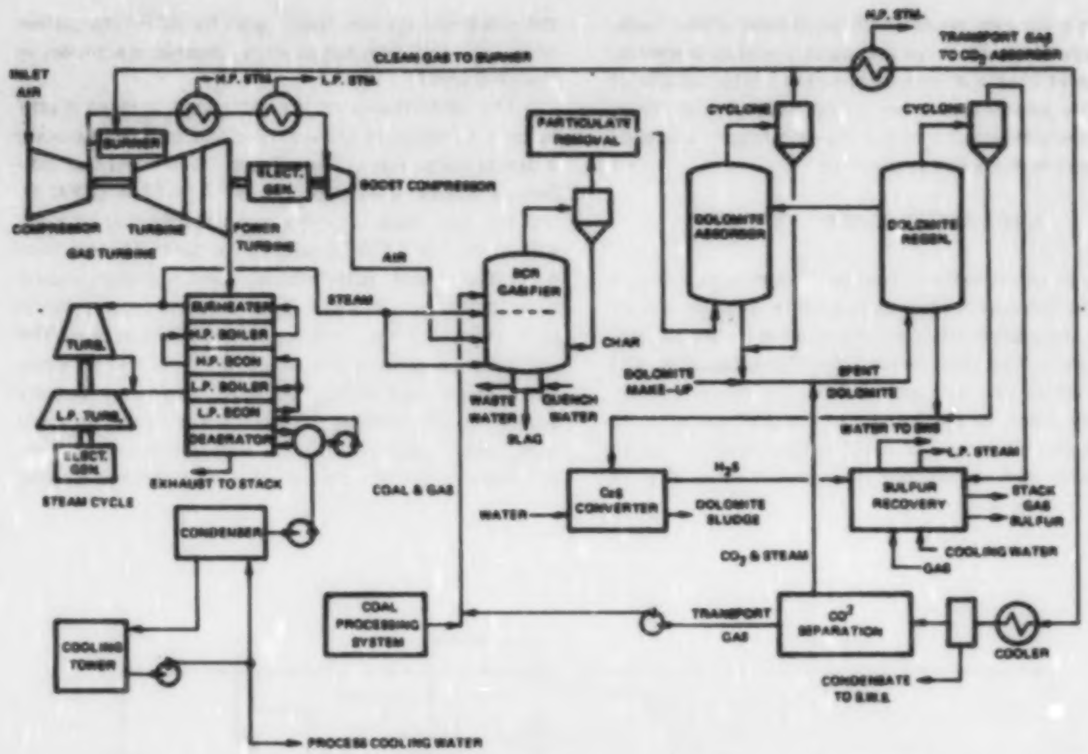

CLEAN GAS TO BURNER
INLET AIR
H.P. STM.
L.P. STM.
BURNER
ELECT. GEN.
BOOST COMPRESSOR
COMPRESSOR
TURBINE
POWER TURBINE
GAS TURBINE
AIR
STEAM
SUPERHEATER
H.P. BOILER
H.P. ECON
L.P. BOILER
L.P. ECON
DEAERATOR
TURB.
L.P. TURB.
ELECT. GEN.
STEAM CYCLE
EXHAUST TO STACK
CONDENSER
COOLING TOWER
PROCESS COOLING WATER
COAL & GAS
COAL PROCESSING SYSTEM
PARTICULATE REMOVAL
BCR GASIFIER
CHAR
WASTE WATER
QUENCH WATER
SLAG
H.P. STM.
TRANSPORT GAS TO CO$_2$ ABSORBER
CYCLONE
CYCLONE
DOLOMITE ABSORBER
DOLOMITE REGEN.
DOLOMITE MAKE-UP
SPENT DOLOMITE
WATER TO SRS
L.P. STEAM
H$_2$S
CaS CONVERTER
WATER
DOLOMITE SLUDGE
SULFUR RECOVERY
STACK GAS
SULFUR
COOLING WATER
GAS
CO$_2$ & STEAM
TRANSPORT GAS
CO$_2$ SEPARATION
COOLER
CONDENSATE TO S.R.S.

Figure 7. Integrated COGAS/BCR/CONOCO system.

upon an iron-oxide process operating at gasifier outlet temperature of 810 K (1000 F). Because of the need to convert the SO$_2$ resulting from the iron-oxide process to elemental sulfur (the preferred form), about 8 percent of the fuel gas must be used resulting in a significant performance penalty.

With the BCR-based systems, a 1700 K (2600 F) turbine temperature was assumed. This temperature is the target goal of an ERDA program to be initiated in early 1976 to develop second-generation gas turbines for utility use. Performance of second-generation integrated systems with both low- and high-temperature cleanup is shown in figure 9. The efficiency of the integrated system with the low-temperature cleanup is comparable to conventional steam stations with flue gas desulfurization (FGD); the systems with high-temperature cleanup are appreciably better.

SYSTEM ECONOMICS

Because of the lower capital costs of the power system, the cost of the gasification and cleanup systems are partially offset when compared to a conventional steam station with FGD. A comparison of the costs of power for the various systems is shown in figure 10. Here it is seen that the first-generation systems (fixed-bed gasifier, 1477 K [2200 F] turbine) are marginally competitive with the steam station. However, second-generation systems (entrained-flow gasifier, 1700 K [2600 F] turbine) are more attractive with the potential

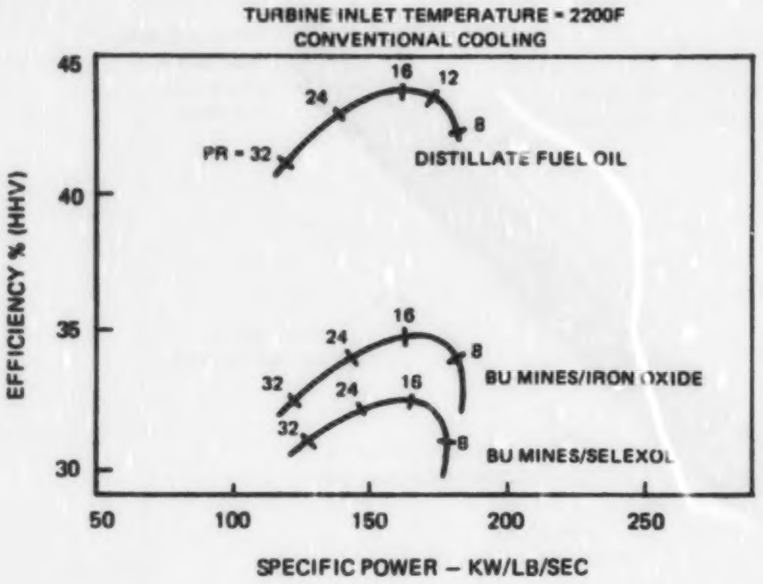


Figure 8. Performance estimate for first generation systems.

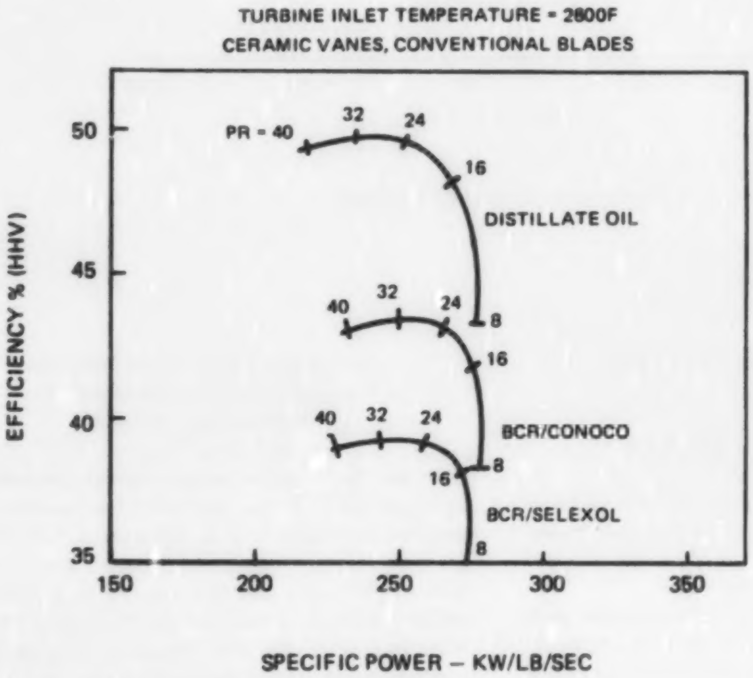


Figure 9. Performance estimate for second generation systems.

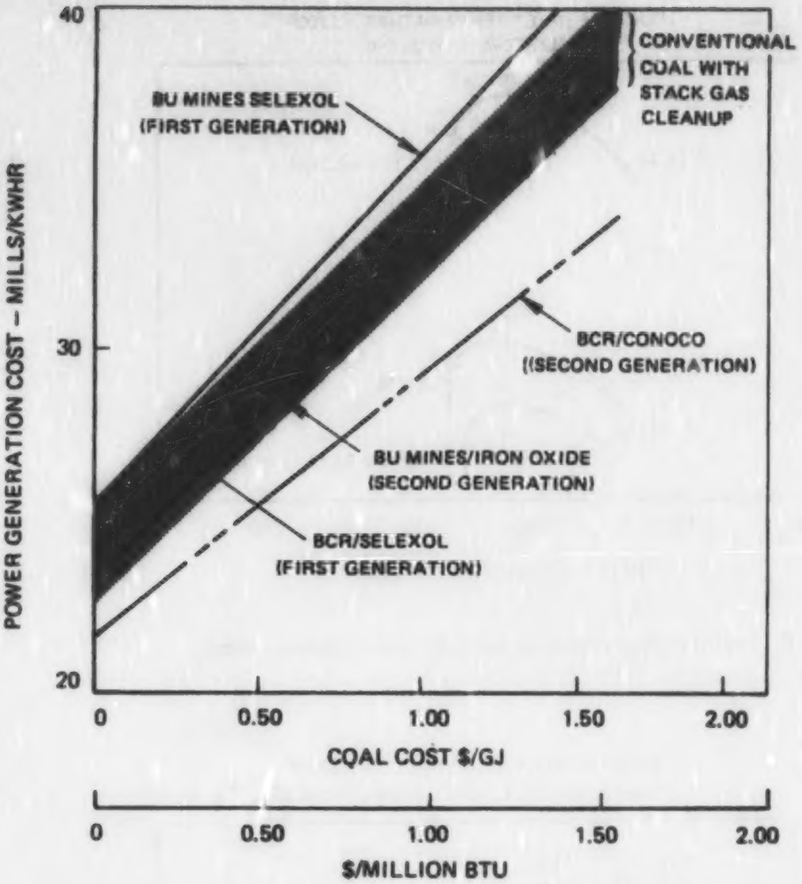


Figure 10. Busbar power cost.

of generating electricity at costs some 15-20 percent lower than the steam station.

ENVIRONMENTAL ASSESSMENT

The foregoing has served to identify the performance and economic potential of integrated power systems. An equally important aspect is the environmental intrusions such a system might have.

The primary guideline used in establishing the goals for the air emissions was that the overall plant would have to meet the regulations for large coal-fired power stations; i.e.,

SO_2 0.52 kg/GJ (1.2 lb/million Btu)
NO_x 0.30 kg/GJ (0.7 lb/million Btu)
Particulates 0.04 kg/GJ
(0.1 lb/million Btu).

Both low- and high-temperature cleanup processes could easily achieve the SO_2 goal with the low-temperature processes being able to go to 100 ppm of H_2S in the fuel gas quite readily. The high-temperature processes varied between 100 ppm and 500 ppm of H_2S, again easily within the limits. Emissions from the stack of the Claus plant associated with each cleanup process were appreciably higher than from the power system stacks, but the sum was still within the limits (see table 3 for the various

Table 3. Estimated environmental intrusion of integrated power systems
(All values in kg/GJ coal unless otherwise noted)*

	Water	Thermal[1]	SO_2	NO_x	Particulate	Solids	Sulfur[2]	Ammonia[2]
BOM/Selexol	94.0[3]	0.005	.138[6]	.153	----	6.28	1.27	0.59
1477 K COGAS	12.0[4]	-----[5]	.038	.075	.004[8]	----	----	----
TOTAL	106.0	0.005	.176	0.228	.004	6.28	1.27	0.59
BOM/Iron Oxide	----	0.018	0.334[6]	.13	---	6.28	1.08	----
1477 K COGAS	12.0[4]	-----[5]	.145	1.41[7]	.03[9]	----	----	----
Total	12.0	0.018	.489	1.54	.03	6.28	1.08	----
BCR/Selexol	224.0[3]	0.016	.209	.129	----	3.05	1.18	0.41
1700 K COGAS	10.0[4]	-----[5]	.034	.005	.004[8]	----	----	----
Total	234.0	0.016	.243	.134	.004	3.05	1.18	0.41
BCR/CONOCO	32.0[3]	0.002	.014	----	---	3.05	1.17	----
1700 K COGAS	9.0[4]	-----[5]	.224	1.34[7]	.02[9]	----	----	----
Total	41.0	0.002	.238	1.34	.02	3.05	1.17	----

---

* 1 kg/GJ = 0.430 lb/million Btu.

[1] GJ's rejected per GJ's coal.

[2] Recovered with no credit for subsequent sale.

[3] See Table 4 for water characteristics.

[4] Includes boiler makeup and cooling tower losses.

[5] Mechanical draft cooling tower losses.

[6] Includes emissions from Claus plant. A 90%+ reduction could be obtained with tail-gas cleanup.

[7] Sum of thermal and fuel-related NO_x.

[8] Assumed to be equal to methane-fired systems.

[9] Sum of carryover and combustion products.

emissions). Additional treatment of these stacks could further reduce the SO_2, but at a cost and performance penalty.

The emissions of NO_x, however, were not as amenable to reduction. The low-temperature processes removed essentially all the fuel-bound nitrogen, thus only the atmospheric NO_x (that resulting from the combination of atmospheric nitrogen with oxygen during combustion) was formed. Because of the low flame temperatures associated with the low-calorific value fuel gas, these emissions are well below those for other fuels. Unfortunately, the fuel-bound nitrogen compounds pass through the high-temperature cleanup processes and, at the concentrations involved, are 90 percent or more converted to NO_x. Thus, these emissions from the integrated system are far above the prescribed value as can be seen in table 3.

The particulate story is somewhat analogous to that for NO_x. Aqueous scrubbing using available scrubber technology in the low-temperature systems removed essentially all the particulates. There are, however, no developed high-temperature particulate removal devices in commercial service capable of removing small ($< 2\ \mu$) particles at the required efficiency. However, it can be postulated that cyclones, followed by granular beds or fabric filters made of high-temperature material, would be capable of 99+ percent removal of particulates to the 2μ level and 90 percent or more in the $<2\mu$ to submicron levels (e.g., see ref. 5). Thus, all the integrated systems considered were assumed able to meet the regulation for coal-fired stations.

In addition to the airborne emissions, there are a number of sources of water-borne and solid wastes from the coal processing system. Perhaps the worst offender would be the fixed-bed gasifier and low-temperature cleanup since, in that instance, a significant amount of coal tars would be present. The chemical characteristics of the process condensates from such a system are given in table 4. According to reference 4, all of the water emissions from the integrated system can be treated so there will be no release of water-borne pollutants and the system could be operated in compliance with the effluent controls currently mandated for 1983 with respect to the Best Available Technology Economically Achievable.

SUMMARY

The integration of coal gasification, fuel gas cleanup and combined-cycle power systems could be realized by the end of this decade using technology currently available or in late stages of development. While this first-generation system would be only marginally attractive in an economic sense, its operation would provide the necessary experience which would lead to higher performance systems.

The second-generation integrated systems which could appear in the mid-1980's would offer higher efficiencies and, possibly, lower capital costs than conventional steam stations with FGD. This would result in lower generating costs, perhaps by 20 percent. With continued research into methods of removing or combusting fuel-bound nitrogen compounds, these systems would also have considerably less environmental intrusion than the steam stations.

Table 4. Characteristics of process condensate from Bureau of Mines/selexol process
(All values in ppm except pH)

Component	
Total Ammonia	200-400
Total Sulfur	
Phenol	500
Thiocyanate	100
Cyanide	1-10
Fatty Acid	
Chloride	500
Carbonate	250
COD	
BOD_5	2500
Sulfides	10-100
Heavy Metals	10-20
pH	9

REFERENCES

1. P. F. H. Rudolph, "New Fossil-Fueled Power Plant Process Based on Lurgi Pressure Gasification of Coal," Proceedings of the Division of Fuel Chemistry, American Chemical Society, May 1970.
2. F. L. Robson and A. J. Giramonti, "An Advanced-Cycle Power System Burning Gasified and Desulfurized Coal," Proceedings of the First Seminar on the Desulphurization of Fuels and Combustion Gases, Geneva, Switzerland, November 1970.
3. L. Shure, "Energy Conversion Alternatives Study (ECAS), Comparison of Task I Results by NASA-Lewis Research Center," May 27, 1975.

4. C. Colton, "Low- and Intermediate Btu Fuel Gas Cleanup," Environmental Aspects of Fuel Conversion Technology II, Hollywood, Florida, December 1975.

5. A. K. Rao et al., "Particulate Removal from Gas Streams at High Temperature/High Pressure," EPA-600/2-75-020, August 1975.

NO_x CONSIDERATIONS IN ALTERNATE FUEL COMBUSTION

G. Blair Martin*

INTRODUCTION

In the search for energy supplies, the United States is projected to place heavy reliance on coal which is the most abundant fossil fuel available. There are many methods of extracting the energy from coal being pursued; however, the ultimate decisions on the path(s) to be followed depend on both economic and environmental considerations. These considerations cover the full range from resource extraction through processing to end utilization. On the economic side it is necessary to include not only capital and operating costs but also the overall energy efficiency of the process. On the environmental side, there are potential impacts in every step and the overall effect on air, water, and land quality must be assessed. For the purposes of this paper, only the end use processes (i.e., combustion systems) will be considered.

The ways in which coal can be used in an environmentally acceptable manner are dependent on the type of combustion source. The pollutant which must be controlled includes sulfur oxides, nitrogen oxides, carbon monoxide, unburned hydrocarbons, and total particulate. Perhaps the most options exist for utility generation of electric power. One option currently being used is the direct combustion of coal with stack gas cleaning for sulfur oxides and particulate and combustion modifications for control of nitrogen oxides, carbon monoxide, and unburned hydrocarbons. Improvement of the existing technology is being pursued by a variety of EPA programs. A second option is the conversion of coal into low sulfur fuels to be utilized in conventional steam boilers or combined cycle plants. The large energy losses currently associated with fuel cleaning processes appear to require use of the advanced design combined cycle with integrated gasifier to achieve energy efficiency comparable to the first option. Major unknowns in these designs are the criteria for minimizing nitrogen oxides and other combustion related pollutants. The third option is the use of fluidized bed combustion to minimize sulfur oxides and other pollutants. The area of sulfur oxides control was the subject of a recent conference (ref. 1) and many excellent papers were prepared. One particularly pertinent summary on fuel conversion processes by Spaite (ref. 2) contained the following conclusion:

> "The competitiveness of low and intermediate Btu gas systems for power plant application appears to depend on a high level of success in development of improved gas turbines, which can be integrated into advanced high efficiency power cycles which compensate for losses suffered in conversion of coal to clean fuels . . . ."

For other applications, such as residential and commercial heating, low-sulfur, high-Btu fuels will be required. Candidates under consideration include synthetic natural gas (SNG), synthetic oils, and alcohol fuels.

This paper will concentrate on combustion and emission characteristics of alternate fuels, an area where information is still very limited. The topics to be covered include a summary of the most recent combustion data for both boiler and gas turbine systems and a presentation of some concepts that may have potential for controlling the formation of NO_x and other pollutants in the combustion process.

BACKGROUND

A wide range of subject matter relates directly to combustion of alternate fuels. The topics include pollutant formation mechanisms, applicable emission control techniques, fuel characteristics, and end use equipment type. Since these areas have been treated in detail for alternate fuels previously (ref. 3), the background presented below is a brief general summary. The most recent information on combustion and emission characteristics is summarized.

Pollutant Formation Mechanisms

The mechanisms of formation of NO_x have been extensively discussed (refs. 4,5,6,7); however, a brief summary is in order. (Note: Subsequent discussion will be limited to nitric oxide (NO) which is the primary form of nitrogen oxides found in the flue gas of conventional combustion equipment.) The mechanisms for formation of NO are as follows:

1. Thermal NO is formed from fixation of atmospheric nitrogen by Zeldovitch reactions which have a strong temperature dependence.

2. Fuel NO is formed by oxidation of chemically bound nitrogen in the fuel by reactions with a low temperature dependence but a strong oxygen availability dependence.

---

*G. Blair Martin is with the Combustion Research Branch, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Proceding page blank

There is also recent experimental evidence (ref. 8) to show that nitrogen specie (e.g., NH_3 and HCN) can be synthesized in fuel rich flames as postulated by Fenimore (ref. 9) and subsequently oxidized to NO as is fuel nitrogen.

Other pollutants such as carbon monoxide, unburned hydrocarbons, and carbon particulates are normally low in well designed conventional systems.

Emission Control Techniques

The basic combustion modification techniques for NO_x control can be summarized as follows:

1. Diluent addition to reduce flame temperature is accomplished through the use of either water or recycled flue gas added to the combustion air;
2. Staged combustion is based on operation of burners at a fuel rich condition with delayed secondary air addition to complete heat release, thereby limiting both peak flame temperatures and primary zone oxygen availability;
3. Burner modifications involve changes in fuel and air mixing conditions to promote localized fuel rich conditions and/or combustion gas recirculation;
4. Novel techniques, such as catalytic combustion, may allow NO emissions lower than those achievable for combustion of clean fuels in conventional systems and may be particularly applicable to redesign for maintaining system efficiency.

The first technique controls only thermal NO, while the last three may also control fuel NO.

The emissions of the products of incomplete combustion (carbon monoxide, unburned hydrocarbons, and carbon particulate) are subject to being increased as NO_x is decreased past a critical point for fixed system design; however, there is a body of evidence that indicates that these emissions can be controlled if the system is designed or modified with NO_x control requirements in mind.

Fuel Characteristics

The fuels of concern are clean liquid and gaseous fuels which can be derived from coal and for which some combustion and emission information is available. The fuels to be considered are discussed below and properties are shown in tables 1 and 2.

Table 1. Comparison of various gaseous fuels

Type of Fuel	Higher Heating Value KJ/M^3 (Dry)	Gas Composition, Mole %						
		CO	H_2	CH_4	C_2H_6	CO_2	N_2	H_2O
Texarkana Natural Gas[a]	36,083	0.0	0.0	96.0	0.0	0.8	3.2	0.0
Cleveland Natural Gas[a]	42,200	0.0	0.0	80.5	18.2	0.0	1.3	0.0
Synthetic Natural Gas Koppers-Totzek[b]	35,896	0.08	2.5	94.2	0.0	0.4	2.8	0.0
Synthetic Natural Gas Lurgi[b]	36,586	0.0	0.8	96.8	0.0	1.2	1.1	0.0
Medium-Btu Gas Koppers-Totzek[b]	11,120	50.4	33.1	0.0	0.0	5.6	0.0	9.6
Medium-Btu Gas Lurgi[b]	11,269	9.2	20.1	4.7	0.5	14.7	0.0	50.2
Low-Btu Gas-Lurgi[b]	6,717	13.9	19.6	5.5	0.0	13.3	37.6	10.1
Low-Btu Gas-Winkler[b]	4,403	19.0	11.7	0.5	0.0	6.2	51.1	11.5
Low-Btu Gas-Hygas[b]	8,806	13.5	16.6	8.4	0.6	12.7	28.9	18.2
Low Gas-U-Gas[b]	5,597	17	11.6	4.1		8.8	45.4	12.0

[a] Handbook of Chemical Engineering, John H. Perry--Editor, 3rd edition.

[b] "Clean Fuels from Coal-Symposium Papers," Institute of Gas Technology, September 10-14, 1973

Table 2. Comparison of various liquid fuels

Fuel	Higher Heating Value KJ/KG	Ultimate Analysis, Weight %					
		C	H	N	S	O	Ash
Distillate Oil[a]	44,892	86.9	13.1	0.023	0.096	0.0	< 0.002
Residual Oil[a]	44,147	86.8	12.5	0.22	0.89	0.0	0.03
COED Crude[b]	--	83.0	8.4	1.1	0.35	7.15	0.0
COED[b] Hydrotreated	--	88.0	11.6	0.01	0.01	0.38	0.0
Synthoil[b]	39,077	89.6	7.6	0.9	0.31	1.6	(1.3)
H-Coal Crude[b]	--	--	9.5	0.68	0.19	--	--
H-Coal Low Sulfur	--	--	8.4	1.05	0.43	--	--
Toscoal Oil[b]	37,681	80.7	9.1	0.7	0.2	9.4	0.2
Shale Oil	43,496	84.6	11.7	1.77	0.76	--	0.01
Alcohol Fuel	22,278	37.5	12.5	0.0	0.0	50	0.0

[a] CRB in-house fuels

[b] "Clean Fuels from Coal-Symposium Papers," Institute of Gas Technology, Sept. 10-14, 1973.

High-Btu Fuels. These fuels are the type which would be potentially economical to transport for use at points remote from the coal conversion sites. Fuels of this type include Synthetic Natural Gas (SNG), alcohol fuels, synthetic coal liquids, and shale oil, for which a number of processes for production are being investigated. These SNG, alcohol fuels, and light synthetic oils can be considered as supplements or replacements for natural gas and light fuel oils and may be used predominantly in combustion equipment currently burning these fuels (e.g., residential, commercial, and small industrial boilers). SNG is produced to be similar to natural gas. The alcohol fuels will be predominantly methanol possibly with up to 10 percent higher alcohol. The heavy synthetic oils may be used as boiler fuels or may be distilled to produce light fuels suitable for turbines or residential furnaces.

Medium-Btu Gas. This is the product of oxygen blown gasifier systems and is currently projected primarily as a synthesis gas for production of SNG and methanol. Its use as a boiler fuel may depend more on economics than technical considerations.

Low-Btu Gas. Although identified by the single term low-Btu gas (LBG), the actual nature of the fuel is as varied as the airblown gasification systems that can be used to produce it. It is projected primarily as a fuel utilized in utility boilers or by industrial parks, either of which could be located close to the gasification site, as long distance transportation is not economical. The actual utilization projected for the LBG depends on the time frame. In the near term it may be used in conventional utility boilers and gas turbines either as retrofit to existing systems or integrated new designs. However, in the long run, combined cycles based on supercharged boilers or high temperature gas turbines as the primary combustion device may predominate. To increase the efficiency of advanced design gasifier systems, there is a strong interest in high temperature H_2S removal processes to provide a clean fuel gas at 810 to 1090K. Again, both economics (capital cost and energy efficiency) and technology may come into play in the final decision.

Trace Constituents. The fate of the sulfur is fairly well considered in most studies of medium- and low-Btu gases, and removal of H_2S and COS is well documented. On the other hand, the fate of the nitrogen content of the coal has received less attention. Farnsworth (ref. 10) shows the final concentration of bound nitrogen specie in the medium-Btu gas after low-temperature cleanup from the Koppers-Totzek process to be less than 1 ppm. On the other hand, there is considerable evidence of the presence of large amounts of NH_3 in the product gases (ref. 11). Robson estimates up to 600 ppm of NH_3 in a low-Btu gas with a low-temperature H_2S cleanup and 3,800 ppm from high-temperature processes under development (ref. 12). It is not clear that these nitrogen compounds could be present in the high-Btu fuels; however, it is quite possible that they be present in the low- and medium-Btu gaseous fuels. Finally, many coal conversion systems producing gaseous fuels also form significant amounts of heavy organic tars, and there is some indication that some of this material may be present in the fuel gas after cleanup. This tar may also contain bound nitrogen compounds (ref. 13).

COMBUSTION AND EMISSION CHARACTERISTICS OF FUELS

Each of the candidate fuels has its own distinct combustion characteristics, pollutant emission potential, and operating constraints. Since these fuels have only recently been considered for widespread application to stationary combustion sources, there is a scarcity of experimental combustion and emission information and these characteristics have not been documented for any practical system operating on these fuels. The most recent available data are summarized below and related information for each fuel is discussed.

Synthetic Natural Gas. The composition of Synthetic Natural Gas (SNG) is normally shown as closely approximating that of natural gas (i.e., principally methane) with all trace contaminants (e.g., H_2S, NH_3) removed. If this is the case, combustion and emission properties are well known and thermal NO control technology for utility boilers is well established.

Alcohol Fuels. The alcohol fuels under consideration are predominantly methanol or mixtures of methanol and higher alcohol. Limited results on combustion of "Methyl Fuel" in an unspecified system as reported by Duhl (ref. 14) show NO levels to be about a factor of 4 less than those for methane. Duhl has subsequently reported on methanol combustion in a 50 MW utility boiler and shows only minor differences in emissions of methanol (about 60 ppm NO) and natural gas (about 75 ppm) at comparable conditions (ref. 15). The author has presented a summary of inhouse and contract research on methanol combustion (ref. 16) and the results can be summarized as follows:

1. For any given condition alcohol fuels produce lower emissions of NO_x than distillate oil, methane, or propane.

2. The NO emissions of alcohol fuels increase as the percentage of higher alcohols increases.

3. The low NO emissions for alcohol fuels appear to be a function of the presence and level of oxygen in the fuel molecule, which can be viewed as a diluent carried in the fuel. The operative mechanism appears to be related to thermal effects of the fuel, latent heat of vaporization, and/or decreased flame temperature; however, chemical effects cannot be totally ruled out.

4. The magnitude of the difference between methanol and any conventional fuel is a characteristic of system design; however, the difference appears to be smaller for cold wall systems.

5. The emissions of CO, UHC, and particulate from alcohol fuels were generally the same as, or less than, those for the conventional clean fuels tested (propane and distillate oil). Aldehydes do not appear to be a significant problem based on limited data.

6. From a technical standpoint, methanol appears to be a satisfactory fuel for stationary combustion systems; however, the final commercial feasibility will probably depend more on cost and availability than on the ability to burn the fuel.

Synthetic Oil Products. The data on combustion of synthetic oils derived from coal and shale containing high levels of chemically bound nitrogen (>1 percent) are very limited; however, some data on combustion of lower nitrogen (<0.5 percent) synthetic oils have been reported by Haebig for a small atmospheric pressure burner (ref. 17) and by Hardin for a gas turbine combustor (ref. 18).

Haebig used a small firebrick chamber, fired by a modified flame retention residential oil burner with an air atomizing nozzle. The heat input rate was a nominal one ml per second of oil. Emissions from three coal-derived fuels were measured and compared to conventional distillate oil. The coal-derived oils consisted of one distilled product with 0.31 percent nitrogen and two full range filtered crudes with about 0.5 percent nitrogen. The trends are similar to those previously reported for doped distillate by Martin (ref. 19) and for petroleum derived residual oils by Turner (ref. 20). One particularly significant point is that the distillate from the full range coal liquids contained 0.31 percent nitrogen, apparently indicating that the nitrogen compounds are considerably lower boiling fractions than those found in conventional crudes where Haebig found only 0.01 percent N in a comparable range distillate. At low excess air levels significantly higher fractional conversion of the nitrogen to NO was observed for the 0.3 percent distillate than for the 0.5 percent N full range crude. It was also observed that when the petroleum-based distillate oil was doped to 0.5 percent N with pyridine, the fractional conversion was more similar to the coal distillate than the full range coal oil. Both of these observations may relate to the volatility of the nitrogen compounds and the ability to control the formation of fuel NO from synthetic oils through combustion control as discussed by the author previously (ref. 3).

Hardin reported the results of combustion of two COED oils (a light fraction and a blend of 20 percent light and 80 percent heavy fraction), of Sea Coal and of JP-4 and 5 fuels in a T63 gas turbine combustor can. The fuel nitrogen contents for the synthetic oils ranged from 0.15 percent for the 20/80 blend to 0.4 percent for the Sea Coal and total NO_x emissions were reported to increase with increased fuel nitrogen. It was also concluded that combustor modification for fuel NO control did not appear promising; however, no specific attempts at modification are discussed. The conclusion is even less surprising if the combustor operated at the very fuel lean conditions stated (i.e., F/A of 0.0117 to 0.022) and with a lean primary combustion zone. The fuel analysis shows 0.19 percent in the light product and 0.13 percent in the heavy product, indicating that for the distilled COED oil the nitrogen also concentrates in the lighter fractions.

Low-Btu Gas. The combustion data on these fuels are also quite limited; however, some additional data have also become available for both boiler and gas turbine type combustors.

The data from the EPA contract with the IFRF have been presented previously (ref. 3); however, to place some subsequent data in context it is appropriate to show these data again. Figure 1 indicates that the simulated low-Btu gas at 298 K and combusted with 105 percent of theoretical air at 573 K resulted in an NO_x emission of less than 4 ppm.

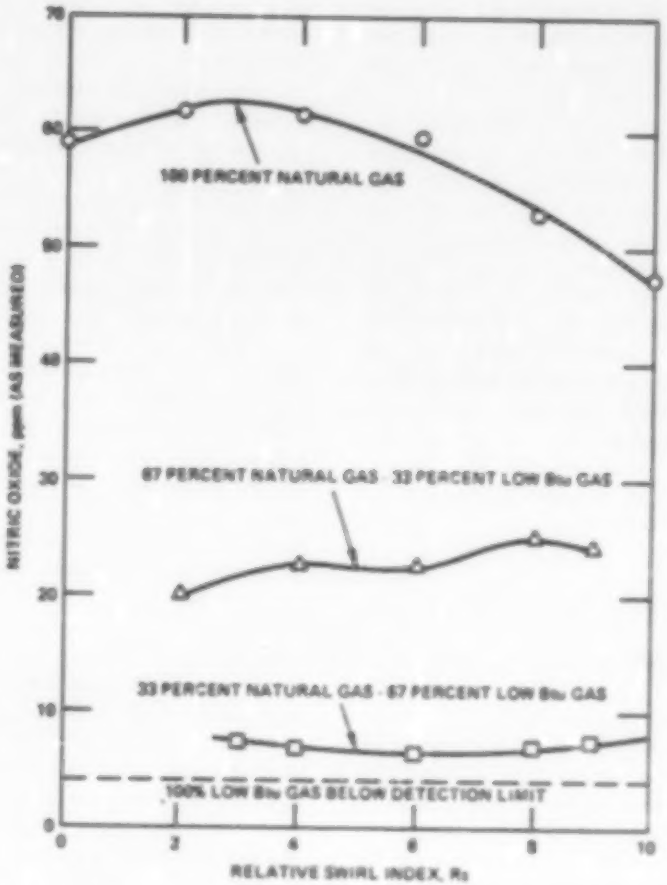


Figure 1. Nitrogen oxide emissions as functions of combustion air swirl and fuel gas composition.

Liesaukas (ref. 13) used a small refractory furnace to burn the product gas from a pilot scale fluid-bed gasifier. The burner was a scaled down version of a bluff body stabilized, register type boiler burner. The fuel gas, from 460 to 1,800 ppm NH_3, was dependent upon the gasifier operating conditions, and was delivered to the burner at temperatures between 305 and 316 K with the organic tar removed in most cases. In one case the NH_3 was scrubbed to the range 11-43 ppm in the fuel gas before combustion to establish the thermal NO baseline. A surprising result is that the baseline level with low temperature fuel and no air preheat is stated to be 90-140 ppm of thermal NO, which is a marked contrast to the IFRF experience. Based on this thermal NO value and the subtraction technique for determination of the fuel NO, the conversion to NO decreases from 65 percent at 240 ppm NH_3 in the fuel gas to 23 percent at 1,800 ppm NH_3. Again the trends are generally similar to those observed for oils (refs. 19 and 20). Although some points in the report by Liesaukas raise questions in the author's mind, this is a particularly valuable contribution of data on combustion of a real coal-derived low-Btu gas containing NH_3.

Pillsbury (ref. 21) has presented results from firing simulated low-Btu gases with heating values from 4,825 to 10,000 KJ/m^3 in subscale and full-size gas turbine can combustors of similar design. The gases were low temperature, bound nitrogen free blends of pure gases. The results show 5 to 25 ppm NO over the combustor exit temperature range of 920 to 1,160 K as compared to 30 to 60 ppm for natural gas over the same range of exit temperatures. The CO was found to be greater than for natural gas in the subscale, but considerably reduced in the full size combustor. These results are similar to those previously reported by Klapatch (ref. 22), although it is unclear in both cases on what basis the NO_x measurements are reported (i.e., ppm as measured, corrected to some O_2 level, etc.).

DISCUSSION

Based on the foregoing summary of available combustion data on alternate fuels, it is obvious that more intensive experience with the actual fuels is still required. A number of systematic studies need to be conducted with specific end use systems in mind. The author's opinion is that efficient, environmentally acceptable use of these fuels may necessitate abandoning or substantially modifying current conceptions of the combustion systems. With this in mind, it is possible to propose some concepts that can potentially form the basis for combustor design experiments and to postulate their success in NO_x control based on existing knowledge and tools. The concepts for combustion of low-Btu gas are discussed in general for boilers and gas turbines and then in detail for gas turbines. The significant properties of synthetic oils are discussed in general.

Liquid Fuels

The same general concepts discussed above should be applicable to combustion of high nitrogen synthetic liquid fuels in boilers and turbines. As previously discussed, the key feature for liquid fuels may be the way in which the fuel nitrogen compounds are bound in the fuel. For conventional petroleum derived heavy fuels, the degree of NO_x control with staged combustion has generally been limited to about 50 percent by the onset of unacceptable smoke formation in the experiments performed to date. It should be noted that some recent results have shown promise for better control by optimizing the burner. On the other hand, experiments with doped distillate oils, where the nitrogen is 100 percent volatile, have resulted in an 80 to 90 percent reduction (see figure 2).

The limited data available on crude and distillate fractions of several synthetic oils derived from coal suggest that the nitrogen compounds may be more evenly distributed over the boiling range of the oil (refs. 17,18,31). This can be seen by reference to table 3.

In the case of a high nitrogen California petroleum crude, the distillate fraction had only about one-tenth the nitrogen concentration of the parent crude. For the three synthetic crudes listed the distillate fuels have 0.6 to 1.45 times the nitrogen content of the parent crude. Necessary information that is not given for any of the fuels is the fraction of the crude that will appear as a light distillate oil. This would allow a better assessment of the "volatility" of the nitrogen compounds in the crude. In any case the comparison indicates that the synthetic oils have significantly more of the nitrogen distributed into the lighter ends and, therefore, may be more amenable to NO_x control by staged combustion.

Low-Btu Gas

It now appears that low-Btu gases will be used predominantly as a low-sulfur fuel supply for utility power generation. The processes used to convert the fuel gas to electric energy will be either conventional steam power plants or combined cycle systems. These combined cycle systems can be either a supercharged boiler with a recovery gas turbine or a fired gas turbine with waste heat recovery boilers. The latter system appears to be favored for advanced gas turbine capable of accepting higher turbine inlet temperature (i.e., >1,590 to 1,640 K). The

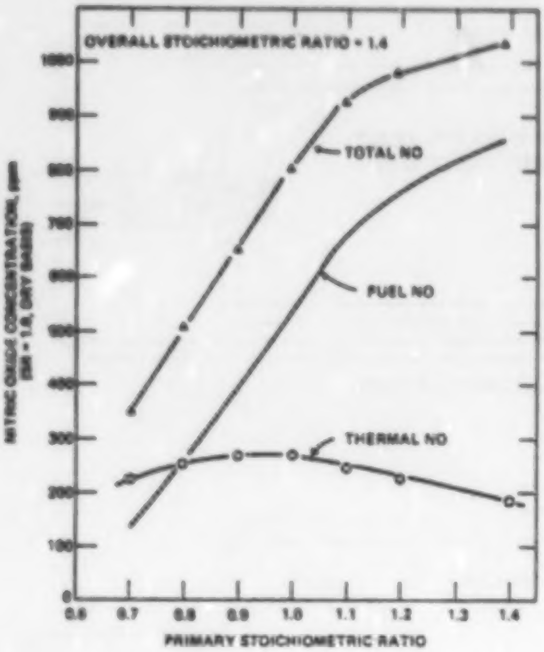


Figure 2. Reduction of fuel NO by staged combustion.

overall system efficiency (i.e., Btu of coal input to Btu equivalent of electricity output) is a function of the product of the thermal efficiency of the gasification system and the thermal to electrical efficiency of the power cycle. The thermal efficiency of gasification systems using low temperature H_2S cleanup systems is in the range of 60 to 70 percent. Combined with a 50 percent efficiency of an advanced generation turbine (i.e., turbine inlet temperatures of 1,813 K) the overall system efficiency is 30 to 35 percent which is less than or equal to a modern coal-fired boiler with SO_2 removal. However, Robson (ref. 23) estimates that this can be raised to 85 percent by using high-temperature H_2S cleanup processes, which yield a 42.5 percent system efficiency with a high-temperature turbine. This points very clearly to the need for consideration of the combustion and emission problems associated with a high temperature fuel gas which may also contain NH_3.

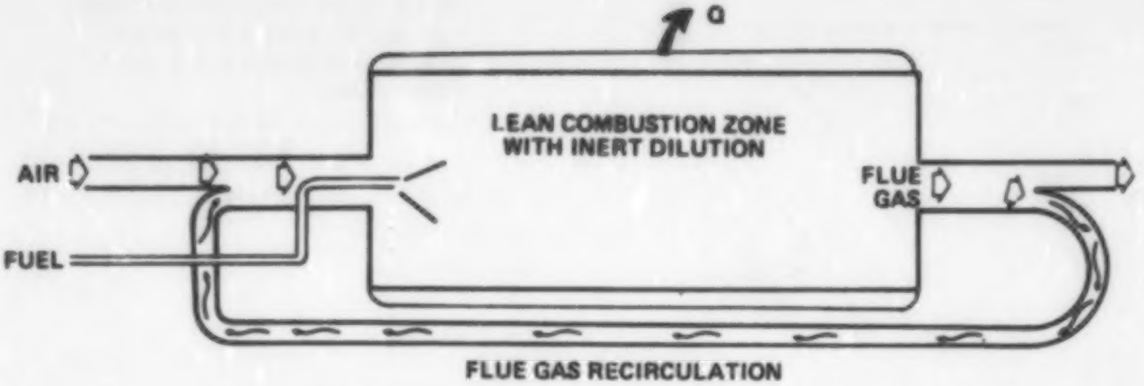
The possible combination to be considered is a complex matrix of fuels (i.e., high and low temperatures, with or without bound nitrogen) and combustion systems (i.e., gas turbines or conventional and supercharged boilers). For the purposes of this discussion, the general types of control strategies for both boilers and turbines are presented below, then one particular set of cases is chosen for more detailed analysis.

Table 3. Comparison of fuel nitrogen content of crude and distillate fractions of synthetic and petroleum crudes

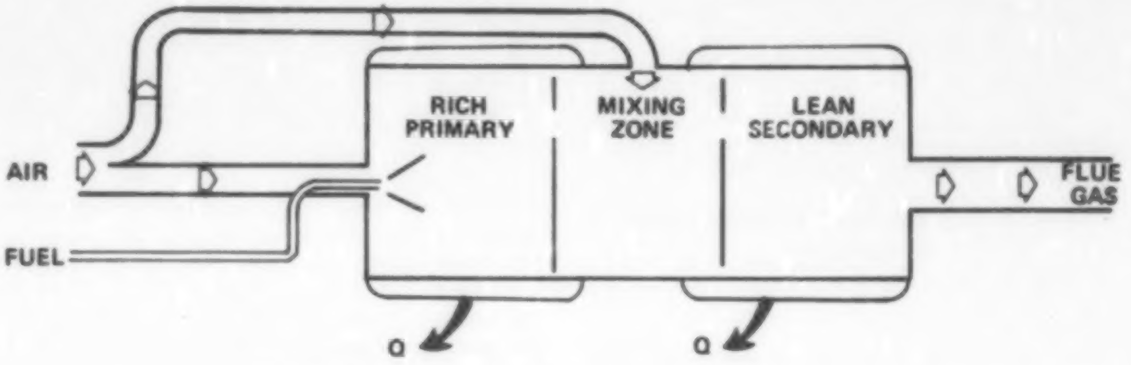
	Nitrogen content %	
Fuel	Crude	Distillate
Wilmington, California, oil (ref. 32)	0.65	0.07
Coal derived (ref. 17)	0.5	0.31
COED coal derived (ref. 18)	0.13	0.19
Shale derived (ref. 31)	2.05	1.60

Boiler Concepts. For boiler applications a key common feature, which gives a great flexibility in designing for emission control, is the ability to remove heat from the combustion gases in a controlled manner and to use that heat in an efficient manner for steam generation. For instance, with a high-temperature fuel gas, the sensible heat could be removed prior to combustion, thereby significantly reducing thermal NO. The systems do require operation with overall excess air as close to stoichiometric as possible to maximize thermal efficiency and this limits the control options somewhat. Two schemes for application of combustion modification to boilers (either supercharged or conventional) are shown in figure 3 and are discussed below:

1. Flue gas recirculation as represented by figure 3A is based on removal of relatively cool combustion gases from the flue for mixing with the incoming combustion air. This reduces the peak flame temperature and controls thermal NO_x. The technique does not affect the total mass of combustion gases to the stack and, if the heat transfer is properly designed, also does not affect stack temperature. As a result the only efficiency impact is the FGR fan power which may be counterbalanced to a degree by an ability to operate at lower excess air.
2. Staged combustion as represented by figure 3B is based on a rich primary combustion zone to limit oxygen availability followed by heat removal and secondary air addition to complete combustion at a lower



A) FLUE GAS RECIRCULATION



B) STAGED COMBUSTION

Figure 3. Conceptual representation of NO_x control techniques for boilers.

peak temperature. The most important feature of this approach is the control of fuel NO_x that can be achieved. Data from a small scale system fired with a distillate oil doped with 1 percent pyridine are shown in figure 2. For this volatile nitrogen compound, the fuel NO_x can be reduced from about 750 ppm for a single staged combustion at a stoichiometric ratio (SR = actual air to theoretical air for complete combustion) of 1.2 to 150 ppm with 0.7 SR in the primary and 1.2 overall. Even for this nonoptimized system with no interstage cooling, the potential for substantial control of fuel NO_x is evident. The presence of interstage cooling should further reduce total NO_x by suppressing thermal NO_x formation in the second stage. These two techniques, combined with optimized design of the burner for the particular technique should provide the basis for control of both thermal and fuel NO_x in boilers.

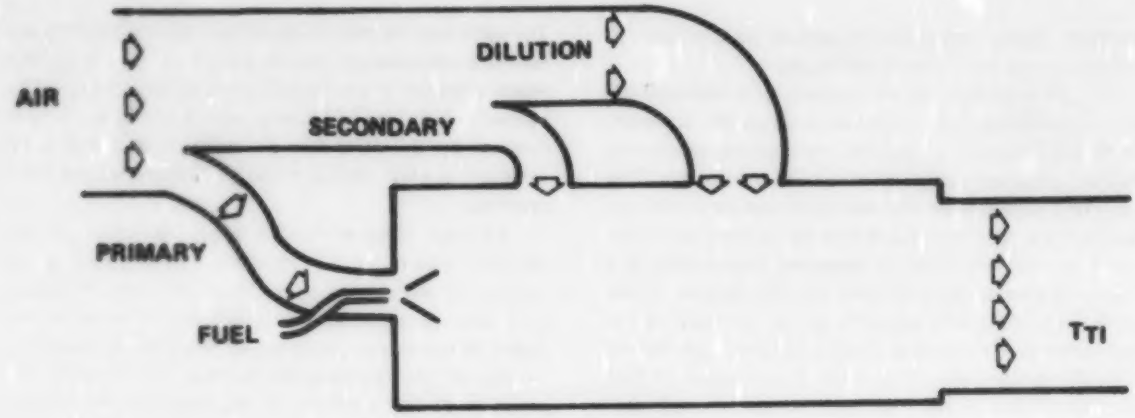
Gas Turbines. The gas turbine has features which are considerably different from boilers and, therefore, requires somewhat different approaches to emission control. A main constraint on the system is the inlet temperature of the hot gas from the combustor to the power extraction turbine. This requires significant quantities of dilution air to be added to combustion gases from the lean primary zone for control of the temperature at the turbine inlet. However, since the efficiency of the turbine increases as the turbine inlet temperature increases, a significant emphasis is being placed on developing power turbines from the current stationary system capability of 1,370 K toward a future goal in the 1,813 to 1,920 K range. There is no heat extraction as such; however, the use of secondary and dilution air to cool the primary zone is a feature that may be used for NO_x control in advanced turbine design. The overall design concepts can be represented in general form in figure 4 and are discussed in more detail below:

1. A schematic of the features of a conventional gas turbine combustor is shown in figure 4A; however, no attempt is made to represent the complex geometrics and air admission patterns of actual combustors. The important features are the near stoichiometric lean primary air and fuel introduced into the primary zone, followed by secondary air to complete combustion and dilution air for temperature control. The features of this system combined with operation at high pressure lead to high combustion intensities and attendant high formation of thermal NO_x. The level of conversion of fuel nitrogen to NO_x is also high for this type of combustor (refs. 18,24). The redesign of this conventional combustor for NO_x control is being pursued by many organizations.

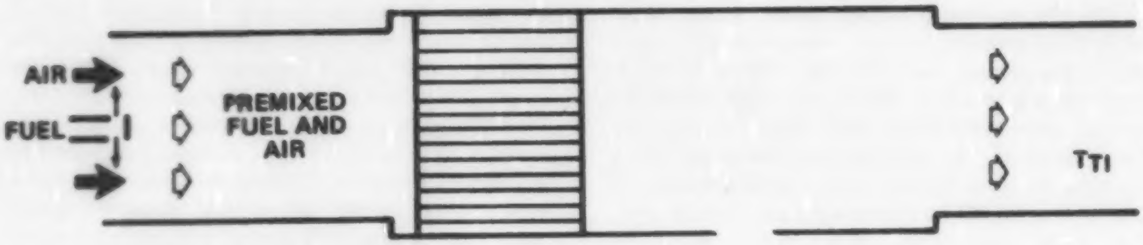
2. An alternative concept based on the use of catalytic combustion is shown schematically in figure 4B. In this concept the total combustion air could be premixed with the fuel, forming a mixture outside the normal flammability limits, then passed into a catalyst bed to promote fuel oxidation. For this stoichiometry the adiabatic flame temperature is relatively low and the rate of thermal NO formation is postulated to be slow. Due to the premixed and oxygen rich nature of the system, high levels of conversion of fuel nitrogen to NO_x can be anticipated. Engelhard Industries' work on catalytically supported thermal (CATATHERMAL®) combustion (ref. 25) indicates that both catalytic surface reactions and homogeneous surface reactions are important in achieving complete combustion and low emissions. Catalyst exit temperatures up to 1700 K with NO_x emissions of less than 7 ppm are reported for a variety of clean fuels including a simulated coal gas. Carrubba (ref. 26) has recently reported 70 to 90 percent conversion of fuel nitrogen to NO_x based on propane doped with NH_3 and a diesel oil doped with pyridine. As previously postulated, this limits the one-stage lean catalytic combustor to use on fuels without bound nitrogen.

3. A concept which should offer the potential for control of fuel NO is shown in figure 4C. Although this system shown is all catalytic for purposes of discussion, other systems using diffusion flame combustors or hybrid conventional-catalytic systems can also be envisioned. The system as shown points out one of the difficulties that must be overcome for practical application, that is, the large volume of secondary air that must be mixed with the primary zone combustion products. The mixing must be rapid to prevent local temperature excursions and the attendant formation of thermal NO_x. The optimum method of secondary mixing to eliminate potential emission and operability problems should be a major emphasis in any development of this concept. The concept also does not show any primary zone heat removal by the secondary air, although this may be a necessary and/or desirable design feature for practical systems.

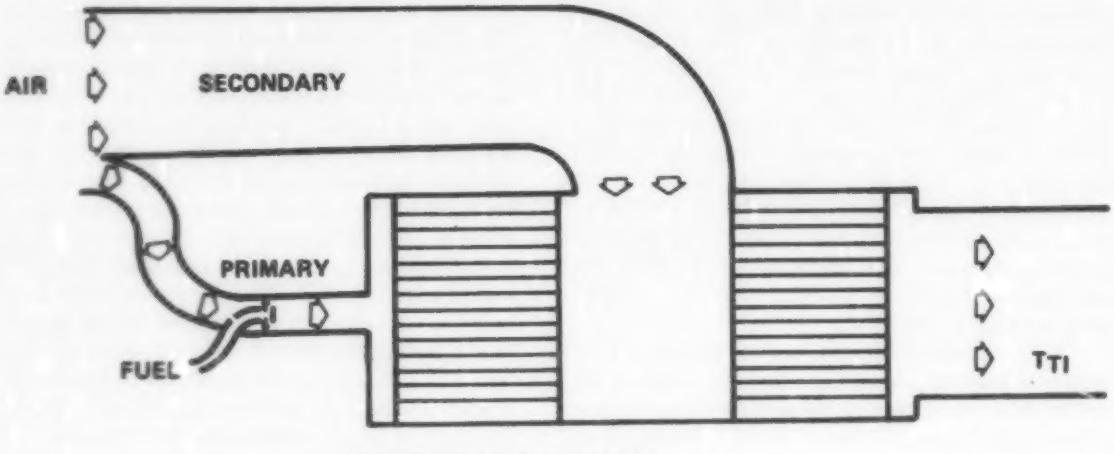
Concept Evaluation. Although the concepts discussed above appear to have strong potential for control of both thermal and fuel NO, data on actual LBG are not available to validate the concepts at the higher temperatures projected for the advanced systems. In view of this, an alternate method of evaluating the emission control potential of the concepts was needed. After some consideration, it was decided that some pseudo-quantitative estimates of emissions could be obtained by using existing mathematical models. The two types of such models are: 1) the fluid dynamic models which include aerodynamic and chemical phenomena; and 2) the stiff chemical kinetics codes with simple stirred reactor and streamtube configurations. Since the geometry of the combustor concepts is completely undefined at this time, it seems unnecessary to do complex aerodynamic calculations until some initial determination of the desired flow properties can be made. For this reason the second approach was chosen. With the emphasis on use of existing technology, the method chosen was the Modular Kinetics Application Program (MKAP) developed by Ultrasystems, Inc., based on the numerical analysis of Tyson and Kliegel (ref. 27). MKAP allows the solution of a large number of simultaneous kinetic rate equations in streamtube (plug flow) and perfectly stirred reactor modes. Complex flow situations can be partially simulated by combining the two reactor modes in various ways. The combination chosen for these calculations was a one-millisecond stirred reactor to achieve ignition, followed by one or two plug flow sections. This configuration was picked because it can be argued that the results of the calculation bear a direct resemblance to one combustor concept, catalytic combustion. The factors to be considered are as follows: 1) in a catalyst monolith each cell may be viewed simplistically as a stream tube; 2) if a significant amount of the reaction occurs in the gas phase as proposed by Pfefferle, the thermal NO_x formation chemistry may be reasonably described by homogeneous kinetics; and 3) for a minimum heat loss from the catalyst, at steady state a nearly uniform temperature may exist over the flow path. This also assumes that the catalyst surface does not play a significant role in the formation or destruction of either fuel or thermal NO. In addition, for this initial evaluation, the calculations were not constrained by one


AIR
DILUTION
SECONDARY
PRIMARY
FUEL
T_{TI}

A) CONVENTIONAL PRACTICE


AIR
FUEL
PREMIXED FUEL AND AIR
T_{TI}

B) SINGLE STAGE CATALYTIC


AIR
SECONDARY
PRIMARY
FUEL
T_{TI}

C) TWO STAGE CATALYTIC

Figure 4. Conceptual representation of NO_x control techniques for gas turbines.

limit imposed by current catalysts, that is, temperature of operation. As the concepts are further developed, this limit must be faced and/or other approaches tried.

The calculations performed represent a first attempt at defining the limit of control of NO_x imposed by chemical kinetics in idealized flow situations and, therefore, should be viewed merely as an indication of potential rather than as a quantitative representation of the achievable emission levels. It should also be emphasized that the practical combustor configurations that might result from these combustor concepts may bear very little resemblance to current practice; however, this in itself should not constitute a barrier to their utilization if practical constraints can be accommodated. It is particularly important to consider that stationary gas turbine combustors are not necessarily constrained by the same factors as aircraft engines (e.g., size and weight). In addition, if the control concepts require, it may be possible to use residence times considerably longer than the 10 milliseconds that approximate current practice for stationary gas turbines.

Having chosen the basic calculation approach, the next step was in choice of the chemical kinetic rates to be used. Again using existing information, the rate data were chosen from the survey performed by Engleman (ref. 28). In an attempt to lend credence to the kinetic rates, the results of the calculation were compared to the jet stirred reactor data of Bartok et al. (ref. 29), for methane with and without added nitrogen species (i.e., NH_3 and NO). With minor adjustment of several rate constants, the same set of kinetics was shown to fit the experimental results of both thermal and fuel NO over the range from 60 to 150 percent of theoretical air (i.e., from fuel rich to fuel lean). It should also be emphasized that in spite of the good agreement between calculated and measured NO values, there are no reported values for HCN from the stirred reactor under fuel rich conditions. The oxidation of this HCN to fuel NO in a lean second stage can be quite significant, as will be shown. The kinetic rates used to predict HCN formation may be questioned, although they fall well within the bounds of current estimates. It should also be noted that the HCN is formed only by CH fragments of the fuel, and does not include synthesis from the initial fuel nitrogen species. The details of the rate selections and comparisons will be documented separately.

Table 4. Composition of Lurgi gas

Constituent	Mole percent
H_2	19.6
CO	13.9
CO_2	13.3
CH_4	5.5
H_2O	10.1
N_2	37.6

An LBG derived from an air blown Lurgi system was chosen for the first series of calculations because of projected near-term availability and, more importantly, the high methane content. The composition of the gas is shown in table 4. For the purposes of this analysis it is assumed that the H_2S is removed from the fuel gas at high temperature (i.e., 1,088 K) by some unspecified process. Following Robson (ref. 12) it was assumed that the gas could contain 4,000 ppm NH_3 following the high temperature cleanup and this value was used in all calculations of fuel NO formation.

Finally, it is necessary to define the combustor inlet and outlet conditions to be studied. The case chosen was a combustor for an advanced gas turbine capable of accepting turbine inlet temperature of 1,813 K with a fuel inlet temperature of 1,088 K and 810 K air at 10 atmospheres. These conditions coupled with 4,000 ppm of NH_3 in the fuel gas and no heat loss from the entire combustor were chosen to represent the most difficult probable case for NO_x control. For these conditions, the overall fuel lean equivalence ratio ϕ (defined as actual fuel to air ratio divided by stoichiometric fuel to air) yielding an adiabatic flame temperature of 1,813 K is 0.45. The results of the calculations for three cases are described below.

1. The first case considered was the single stage lean combustion case for the fuel gas without NH_3. The calculated thermal NO as a function of plug flow residence time is shown in figure 5. It should be noted that the presence of the one millisecond stirred reactor for ignition results in about 23 ppm of NO at the start of the plug flow for the 10 atmosphere case and 7 ppm at one atmosphere. The thermal NO then increases linearly with residence time for both cases; however, the high pressure case increases more rapidly. This points out two factors that should be carefully considered in future studies. First, it cannot be assumed that the thermal NO kinetics at 1,813 K are too slow to be significant, and second, great care must be taken in using low pressure results to infer thermal NO at high pressure for this temperature level. It is also important to point out that for a residence time that might be experienced in an

actual combustion (i.e., 100 ms) the thermal NO level is about 87 ppm corrected to stoichiometric. This appears to be a very favorable result considering the severity of the conditions chosen.

2. The second case was identical to the first except that the fuel gas contained 4,000 ppm of NH_3. It is not particularly surprising that 86 percent of the NH_3 was converted to fuel NO (i.e., about 890 ppm NO as calculated). The calculation indicates that the conversion occurred in the ignition stirred reactor and the first few milliseconds of the plug flow. This is considerably more rapid than the formation of the thermal NO in the same system. It should be noted that the calculation also compares very well with the 70 to 90 percent conversion of

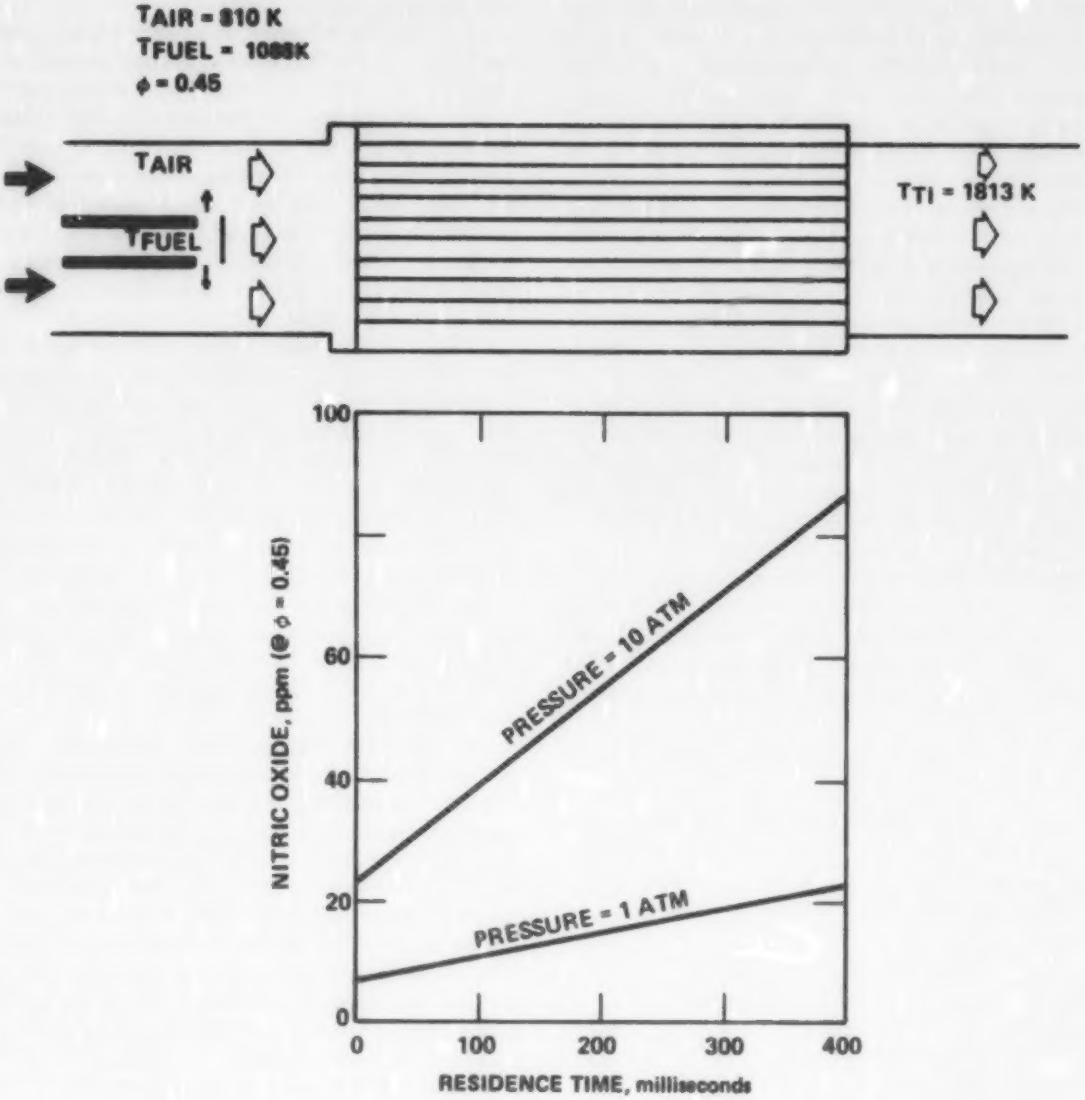


Figure 5. Formation of thermal NO as a function of plug flow residence time.

fuel nitrogen to NO in a lean catalytic converter previously discussed (ref. 26). This result also reconfirms the postulate that fuel NO requires a different control approach than thermal NO and leads to the next calculation.

3. The final case was the two stage concept with the rich primary zone to control fuel NO followed by secondary air addition to achieve fuel burnout. This concept has a much larger number of variables that must be explored to determine the optimum condition, including: primary zone equivalence ratio; primary zone residence time; and the rate of secondary air mixing with the partially burned primary zone gases. For fuel NO control the primary zone is expected to be the dominant feature of the concept. The goal is to maximize the conversion of the fuel nitrogen specie to molecular nitrogen which will have a negligible effect on the NO formation in the second stage and, thereby, minimize the residual nitrogen species (e.g., NO, HCN, NH_3) that result in fuel NO in the exhaust of the second stage. For the chosen input conditions the two key factors in this are the equivalence ratio and residence time of the primary zone. (It should be noted that the temperature of the primary zone and the fuel composition may also have an effect; however, for this study they were not considered.) The results of the calculation are summarized in figure 6. It should be noted that the curve connecting $\phi = 0.45$ and $\phi = 1.33$ is hypothetical but that the shape is based on experimental observations that fuel nitrogen conversion is relatively independent on the fuel lean side until the equivalence ratio approaches unity. The term residual nitrogen specie is the sum of all major nitrogen compounds (i.e., NO, HCN, and NH_3) in the rich primary that can result in NO_x formation upon secondary air addition. The total residual nitrogen species decrease rapidly as the equivalence ratio becomes rich; however, a minimum shown by these calculations occurs at $\phi = 1.33$ for all residence times. As the equivalence ratio increases toward 2, the residual nitrogen species increase for all residence times; however, the increase is progressively larger for shorter residence times. The reason for this can be seen by reference to figures 7 and 8. Figure 7 for ϕ of 1.33 shows that the NH_3 has disappeared very early in the plug flow, while NO and HCN from the exit of the stirred reactor decrease steadily toward equilibrium levels as residence time increases. Figure 8 for ϕ of 2.0 shows a high NH_3 concentration and a moderate NO concentration of the exit of the stirred reactor, both of which decrease significantly with time; however, the concentration of HCN shows a significant increase with residence time. [It should be noted that subsequent calculations have shown that removal of the methane content of the fuel essentially eliminates the HCN formation. If this is borne out by subsequent experimental studies, it may have a significant influence on the ultimate level of fuel NO_x control achievable by staged combustion for fuel gases of varying CH_4 content.] The hot partially oxidized fuel gas containing residual nitrogen species can then be used as the input to the second stage operating fuel lean overall to complete combustion of the fuel. It may be expected that the residual nitrogen species will go predominantly to NO_x in this second stage if very rapid mixing with the secondary occurs.

Since the credibility of the overall results depends heavily on the validity of the calculation of the effluent nitrogen species from the rich first stage, it is necessary to seek some experimental data for comparison. As previously mentioned, most data on fuel nitrogen conversion as a function of equivalence ratio in simple systems have measured only NO and not the other residual compounds on the fuel rich side. In addition none of the measurements have been made at elevated pressure, although the results of the calculations on the fuel lean side indicates that pressure has a very small effect on the conversion. For this reason two comparisons were chosen: 1) the author's data on staged combustion of a doped distillate oil previously presented in figure 2; and 2) recently reported data of Axworthy et al. (ref. 30), performed on a low pressure methane flat flame doped with NH_3 and HCN. The details of the systems and conditions are presented in table 5. For the oil-fired experimental furnace it may be argued that the residual nitrogen species from the rich primary are essentially completely converted to NO_x in the second stage and that measured NO_x constitutes a valid measurement of the residual nitrogen species from the primary. In the case of the Axworthy results only NO is reported; however, recent results in the same system indicate that at 25 ms NO is essentially the only species of importance even under rich conditions. In this low-pressure flat flame, argon was substituted for nitrogen in the inlet mixture, thereby eliminating thermal NO. The comparison of these results is shown in figure 9. First, note that the premixed flat flame data correspond quite well with the calculation at ϕ of 0.45 but diverge substantially on the fuel rich side. This could be a function of at least four differences between the systems: 1) the fact that the flat flame burner is operated with pure methane which may significantly influence the HCN in early parts of the flame; 2) the flat flame has a much shorter residence time and the NO concentration may not have relaxed to the same extent as the longer residence time calculation; 3) the flat flame is nonadiabatic, which may affect specie concentration as related to 2 above; and 4) on the fuel rich side the initial stirred reactor of the calculation may play a dominant role. Second, note that

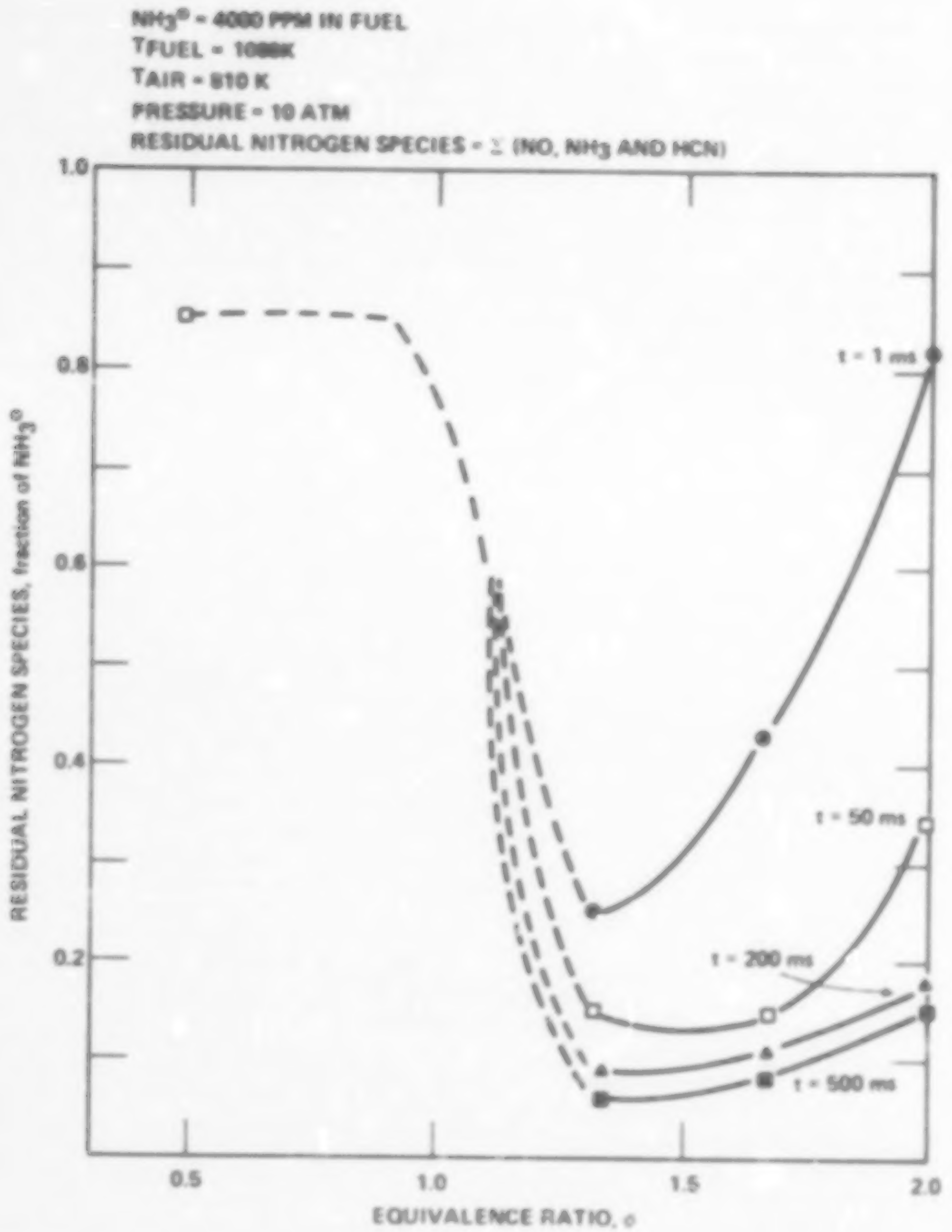


Figure 6. Residual nitrogen species as a function of equivalence ratio and residence time.

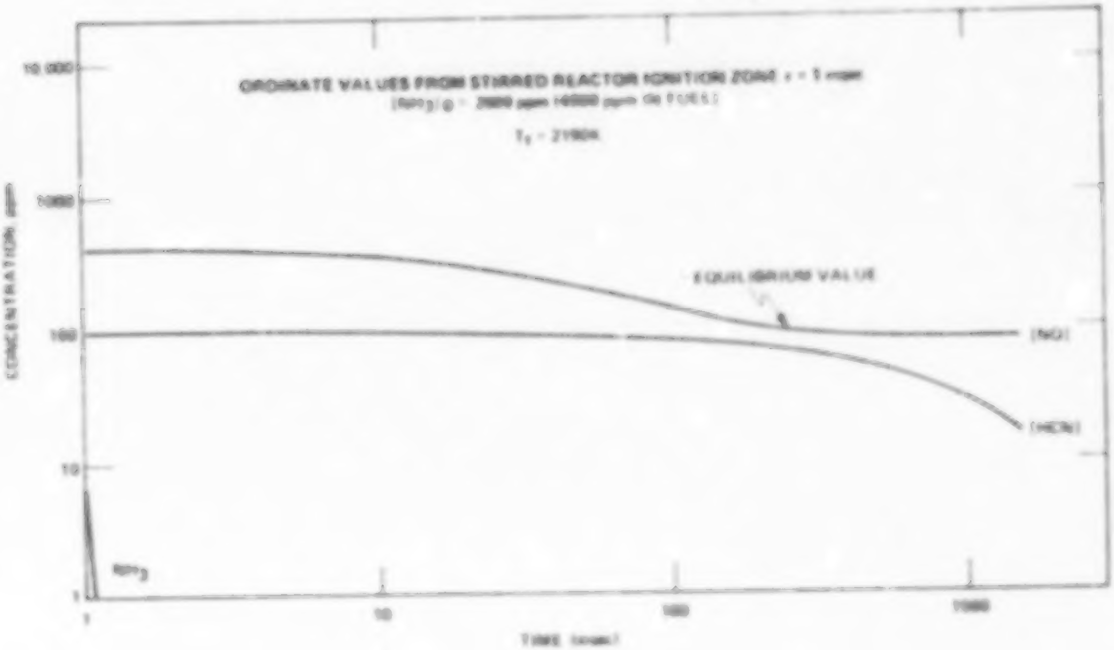


Figure 7. Nitrogen species concentration as a function of residence time at equivalence ratio of 1.33.

on the lean side, the staged system with the diffusion flame primary shows a much lower level of conversion than the estimated trend of the calculation, which is consistent with trends in experimental results on conversion of fuel nitrogen in premixed and diffusion flame systems. However, on the fuel rich side, these results compare remarkably well with the calculations. A most interesting feature is that the author noted a tendency for the NO_x to level off sharply or even turn up as the primary zone equivalence ratio of the staged system was pushed below 1.43. Perhaps the most important aspect of these comparisons may be in the guidance that they may provide for future combustor design exercises that will be undertaken. In any event, in spite of wide system differences, the comparisons lend sufficient credence to the calculated residual nitrogen values, to use them as a basis for the next step in evaluation of a staged system.

Working from the rich primary calculation, several cases were calculated for secondary air injection to achieve the overall lean equivalence ratio of 0.45 and a final temperature of 1,813 K. It was anticipated that the manner in which the secondary air was added would have a significant effect on the thermal NO produced in the second stage burnout zone. If the air is mixed gradually the burnout will occur over a distribution of temperatures from the inlet value, through the adiabatic temperature at ϕ equal unity, to the final value. If the air could be mixed instantaneously with the primary zone product, the temperature would increase to a final value at which little thermal NO is formed.

For the first attempt, a primary ϕ of 2.0 and a 500 msec residence time primary zone was chosen. The secondary was calculated on the basis of instantaneous mixing and a gradual mixing with air mass distribution over 55 msec. These represent two rather extreme cases for purposes of comparison. It must be realized that instantaneous mixing is not possible and that 2 to 3 milliseconds is the shortest known time achieved in experimental attempts to date. It is expected that the thermal NO excursion for these times will be closer to the instantaneous result than to the 55 ms one. This is another parameter subject to further evaluation and optimization. The results are shown in figure 10. The gradual mixing case produces the large expected temperature excursion with the attendant high rate of formation of thermal NO as well as oxidation of the residual

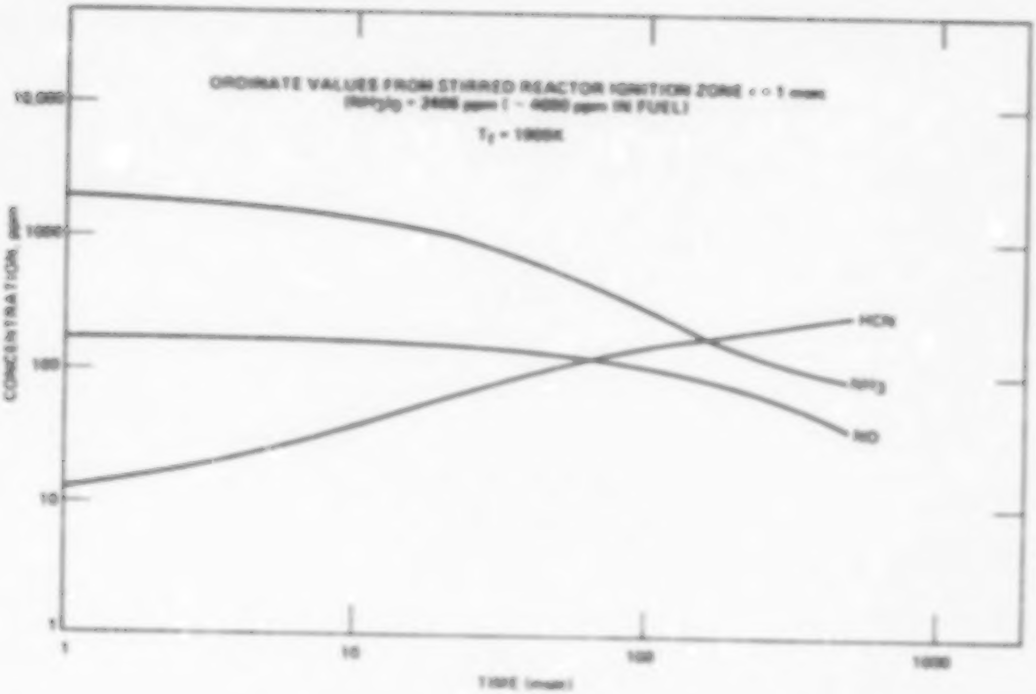


Figure 8. Nitrogen species concentration as a function of residence time at equivalence ratio of 2.0.

Table 5. Comparison of systems

System[a]	Pressure atm.	Fuel	Nitrogen compound	Fuel nitrogen concentration[c]	Primary equivalence ratio range	Overall equivalence ratio	Estimated primary zone residence time milliseconds
1	0.1	Methane	NH_3 or HCN	1540-5000[b]	0.5 to 1.5	Same	25
2	1.0	Distillate oil	Pyridine	1550	0.715 to 1.43	Constant at 0.715 or 0.835	250
3	10.0	Low-Btu gas	NH_3	2000	0.45 to 2.0	Same	200

[a] 1. Low pressure flat flame (ref. 30) - Argon substituted for nitrogen in oxidizer
2. Experimental furnace with rich primary and lean secondary (ref. 19)
3. Calculations for this paper

[b] Constant 2500 ppm in fuel and air for φ = 1.5 to 0.5

[c] Shown as ppmNO for 100% conversion corrected to φ = 1.0

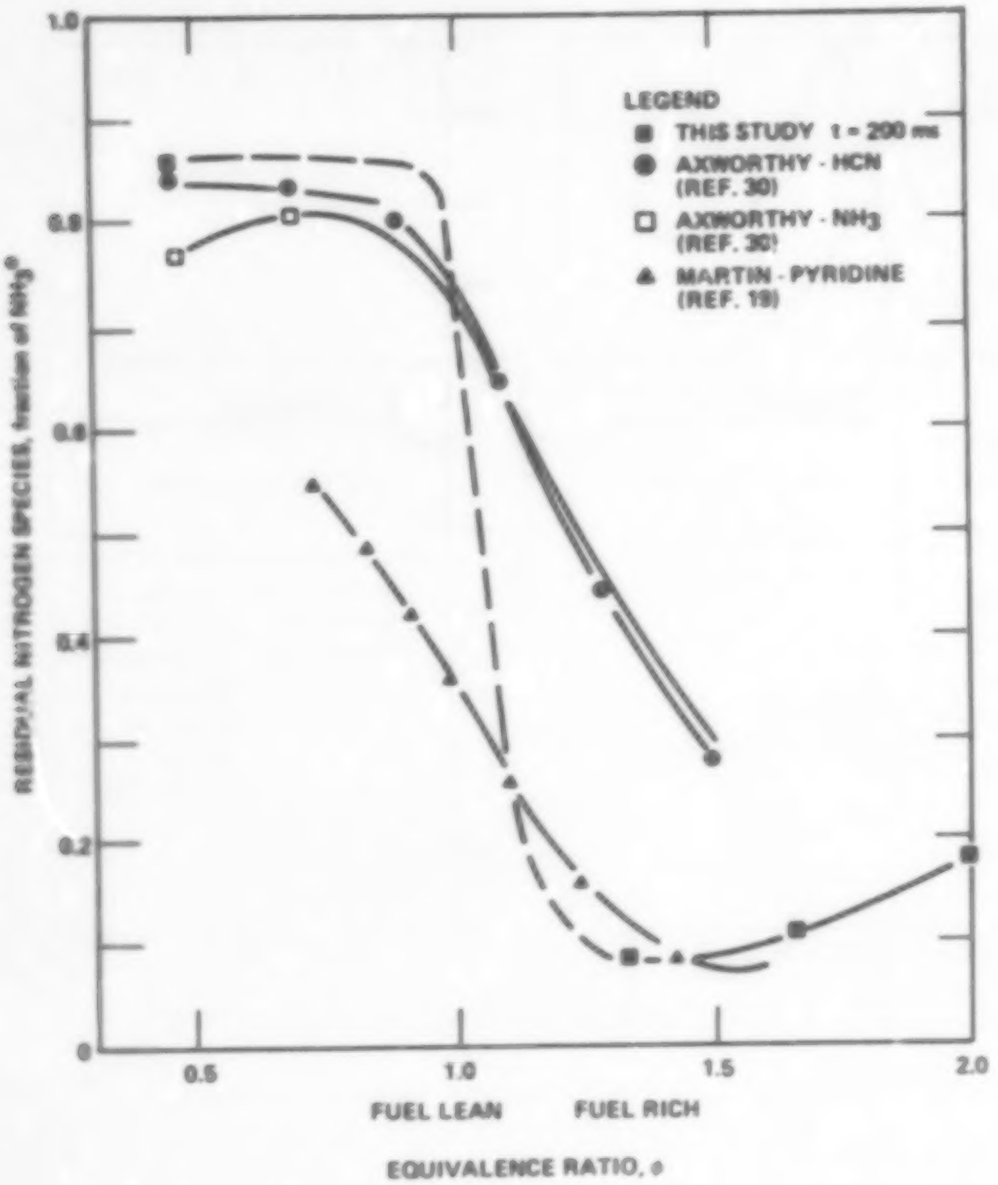


Figure 9. Comparison of calculations and experimental results of other studies.

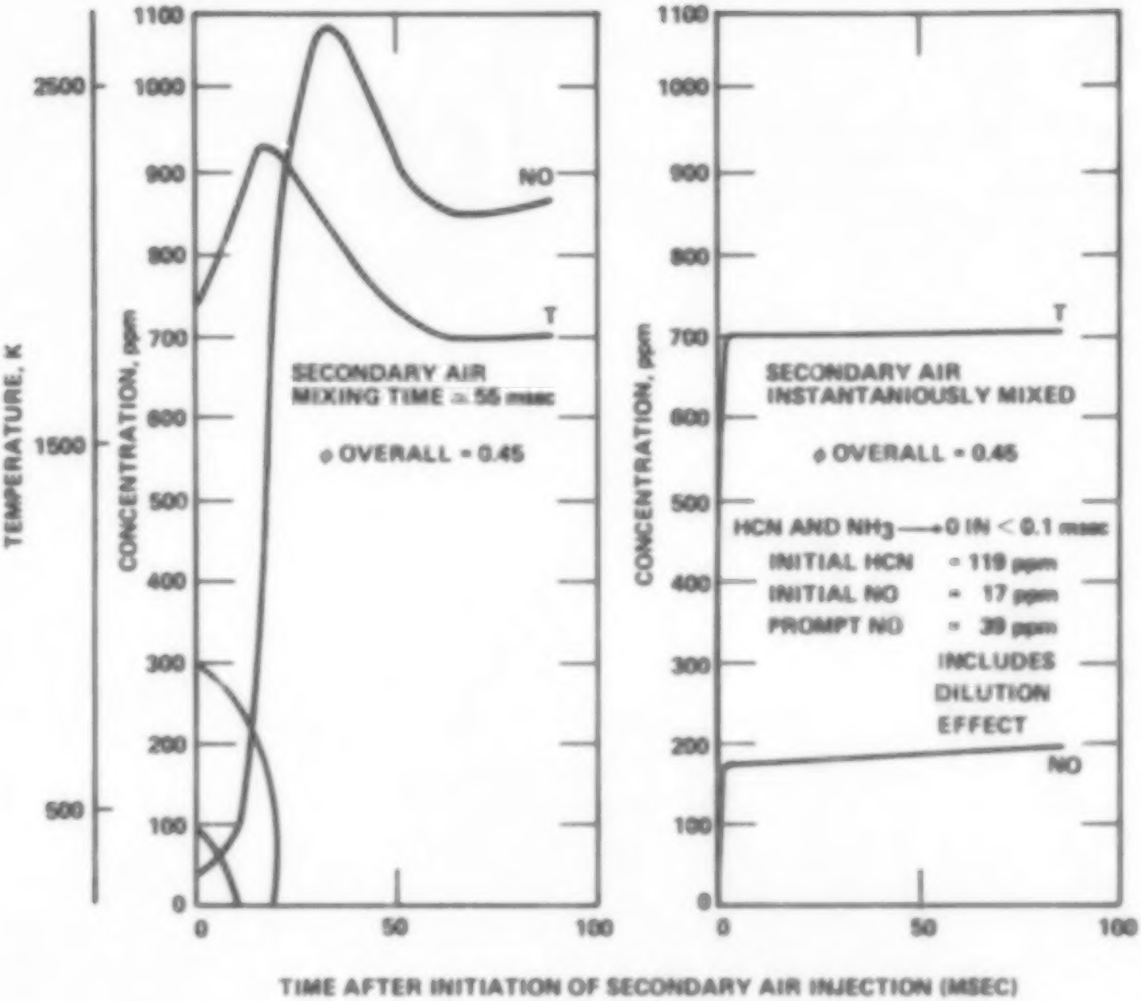


Figure 10. Comparison of instantaneous and gradual mixing of secondary air with primary zone products at $\phi = 2.0$.

nitrogen species from the primary. The instantaneous mixing case produces very rapid conversion of the residual nitrogen specie as well as a small thermal NO spike identified as "prompt NO," followed by a gradual rise of thermal NO with time. In the latter case a final value of 200 ppm NO is approached, which corresponds to approximately 450 ppm NO corrected to stoichiometric. This level of NO is about the same as that of the current state-of-the-art for direct coal combustion; however, there appears to be the potential to achieve even low NO_x with further design optimization.

A second case was chosen based on a primary equivalence ratio of 1.33, and 500 msec at which the residual nitrogen species were a minimum, followed by instantaneous mixing of secondary air to achieve an overall equivalence ratio of 0.46. The results of this calculation are shown in figure 11. The final NO value in the exhaust is 67 ppm at ϕ of 0.46 or about 150 ppm corrected to ϕ of unity. This is a factor of 3 improvement over the first case ($\phi = 2.0$) with instantaneous mixing.

Summary. The results of the calculations indicate that advanced combustor designs have a good potential

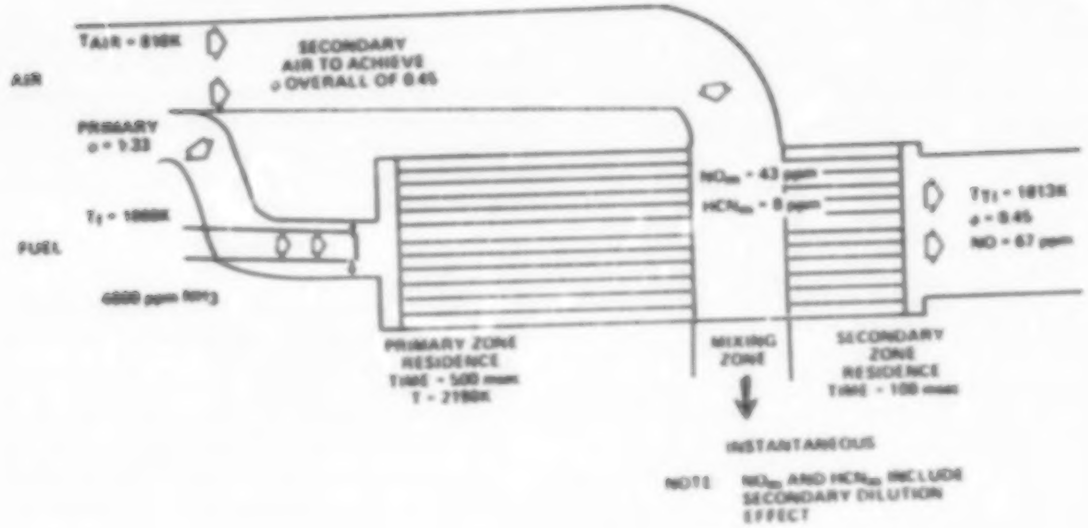


Figure 11. Optimization of the initial design concept.

for controlling total NO_x from a high temperature, nitrogen containing low-Btu gas. It should be emphasized that the results shown here are a very limited set and in no way can be interpreted as representing an optimized application of the technology. However, they are sufficiently encouraging to pursue both the calculation and experimental verfication of the concepts. Some limits of the calculations should be reemphasized as follows:

1. The flow schemes were simplified based on the catalytic combustion scheme represented as a plug flow reactor with only homogeneous reactions influencing NO_x formation. It must be pointed out that the adiabatic temperature for both of the rich primary cases exceeded the postulated maximum allowable bed temperature of 1813 K (i.e., for φ of 1.33, the adiabatic temperature is 2190 K). At these elevated temperatures the catalyst and monolith degradation is a severe problem; however, if only a hot noncatalytic surface is needed at elevated temperatures, some of the high temperature monoliths may serve.

2. Related to the above is the fact that all calculations were done under adiabatic conditions, whereas, in practical turbines there is some heat removal from the primary zone by secondary and dilution air. The nonadiabatic cases need to be considered for at least two reasons. First, the temperature of the primary zone may affect some of the fuel nitrogen species reactions, especially the HCN formation. Second, proper use of primary zone cooling could significantly relax the requirement for instantaneous secondary air addition to minimize mixing zone thermal NO_x.

3. Some of the chemical kinetic rates have not been validated by experimental data, especially for HCN formation.

4. The calculations have been run for only one fuel gas composition. It is quite important to establish the effect of different compositions, especially methane content, on the results.

5. Only a single set of input conditions (i.e., fuel temperature, air temperature, NH_3 content, etc.) has been run.

6. The initial stirred reactor has only been run at one residence time (i.e., one millisecond); however, it appears to play a major role in the fate of fuel nitrogen species. The effect of residence time needs to be evaluated.

7. Alternate concepts, such as a diffusion flame preburner followed by a rich plug flow relaxation zone, may offer even greater potential for NO_x reduction.

It is obvious that extensive work needs to be done to validate these concepts for advanced gas turbine designs.

In addition, similar concepts should be applicable to steam generators with equal or greater success. The most closely related steam generator would be the high pressure (supercharged) boiler; however, with the exception of size, the general approaches should be applicable to all boilers. As previously mentioned, the boiler application may be somewhat easier to accomplish as significant quantities of heat can be removed from the primary zone. This is particularly essential when the boiler must operate at low overall excess air for optimum efficiency. Otherwise, even with instantaneous secondary air mixing, the second stage temperature would be high and significant thermal NO formation could occur.

CONCLUSIONS

Based on the information presented in this paper, the following conclusions were drawn:

1. The data on emission levels and control techniques for synthetic fuels combustion are still very limited; however, some experimental information is now available. The same statement is true for the fuel properties. Additional data are required on both aspects of the problem.

2. In the absence of hard data, an existing computational method was used to estimate the potential of LBG combustor design concepts for NO$_x$ control. The results of those calculations show the potential for over 90 percent control of fuel NO for a high temperature, ammonia containing low-Btu gas is theoretically possible. While these estimates cannot be taken as being quantitative, it is believed that they provide a good indication for the potential of the concepts. The achievable results are obviously limited by practical considerations including size, cost, mixing, and material constraints and duty cycle requirements.

3. A more extensive study is required to examine the effect of other variables and design concepts on NO$_x$ emissions and, thereby, "optimize" the techniques for relatively simple flow systems. This needs to be followed by an experimental evaluation to verify the techniques. The author plans to pursue this line of R&D.

4. Perhaps the most important point is that the combustor design concepts here represent a significant departure from current gas turbine combustors; however, it *may be* necessary to abandon conventional approaches in order to control NO$_x$ emissions for the severe conditions imposed by the advanced power generation systems.

5. While control of NO$_x$ emissions for high-nitrogen synthetic liquid fuels was not specifically considered, it appears that similar concepts should apply. The major uncertainties are in the area of fuel properties as related to smoke formation and/or particulate resulting from solid material remaining in the fuel following refining. If combustion control of fuel NO$_x$ can be used, it will reduce the necessity for hydrotreating of the synthetic fuels to remove nitrogen compounds.

ACKNOWLEDGEMENT

The author wishes to acknowledge the thought and effort devoted by Drs. T. J. Tyson and M. P. Heap of Ultrasystems, Inc., to performing the kinetic calculations and their judgment employed in modifying some of the conditions run in the optimized mode. The author takes sole responsibility for the interpretations placed on those calculations.

REFERENCES

1. Economic Commission of Europe Second Seminar on Desulfurization of Fuels and Combustion Gases, Washington, D.C., November 11-20, 1975.
2. P. W. Spaite, "Liquefaction and Gasification of Solid Fuel Prospects for Production of Synthetic Boiler Fuels from Coal," introductory report presented at Economic Commission of Europe, Second Seminar on Desulfurization of Fuels and Combustion Gases, Washington, D.C., November 11-20, 1975.
3. G. B. Martin, "Environmental Considerations in the Use of Alternate Fuels in Stationary Combustion Processes," symposium proceedings; *Environmental Aspects of Fuel Conversion Technology*, EPA-650/2-74-118, NTIS No. PB 238-304/AS, October 1974, pp. 259-276.
4. W. Bartok et al., "Systems Study of Nitrogen Oxides Control Methods for Stationary Sources, Vol. II," Esso Research and Engineering, Linden, New Jersey, Report GR-2 - NOS-69, prepared for Division of Process Control Engineering, National Air Pollution Control Administration, EPA No. APTD 1298, NTIS, No. PB 192-789, November 1969.
5. R. A. Brown et al., "System Analysis Requirements for Nitrogen Oxide Control of Stationary Sources," Aerotherm-Acurex Corporation, EPA-650/2-74-091, NTIS No. PB 237-367/AS, September 1974.
6. G. B. Martin, "Overview of U.S. Environmental Protection Agency's Activities in NO$_x$ Control for Stationary Sources," presented at the Joint U.S.-Japan Symposium on Countermeasures for NO$_x$, Tokyo, Japan, June 28-29, 1974.
7. D. G. Lachapelle, J. S. Bowen, and R. D. Stern, "Overview of Environmental Protection Agency's NO$_x$ Control Technology for Stationary Combustion Sources," presented at the 67th Annual AIChE Meeting, Washington, D.C., December 1974.
8. K. Yamagishi et al., "A Study of NO$_x$ Emissions Characteristics in Two Stage Combustion," presented at the 15th Symposium (International) on Combustion, Tokyo, Japan, August 1974.

9. C. P. Fenimore, "Formation of Nitric Oxide in Premixed Hydrocarbon Flames," 13th Symposium (International) on Combustion, Salt Lake City, Utah, August 1970.
10. J. F. Farnsworth et al., "Clean Environment with Koppers-Totzek Process," symposium proceedings; *Environmental Aspects of Fuel Conversion Technology*, EPA-650/2-74-118, NTIS No. PB 238-304 AS, October 1974, pp. 115-130.
11. A. J. Forney et al., "Analyses of Tars, Chars, Gases and Water Found in Effluents from the Synthane Process," symposium proceedings; *Environmental Aspects of Fuel Conversion Technology*, EPA-650/2-74-118, NTIS No. PB 238-304/AS, October 1974, pp. 107-113.
12. F. L. Robson and A. J. Giramonti, "The Environmental Impact of Coal-Based Advanced Power Systems," symposium proceedings; *Environmental Aspects of Fuel Conversion Technology*, EPA-650/2-74-118, NTIS No. PB 238-304/AS, October 1974, pp. 237-257.
13. A. Lisauskas and S. A. Johnson, "NO_x Formation During the Combustion of Low Btu Gas from Coal," presented at the AIChE 80th National Meeting, Boston, Massachusetts, September 7-10, 1975.
14. R. W. Duhl and T. O. Wentworth, "Methyl Fuel from Remote Gas Sources," presented at 11th Annual Meeting of the Southern California Section AIChE, Los Angeles, California, April 1974.
15. R. W. Duhl and E. Allegrini, "Methyl Fuel - A Boiler Alternate" presented at the Symposium on Impact of Methanol on Urban Air Pollution, 80th National AIChE Meeting, Boston, Massachusetts, September 7-10, 1975.
16. G. B. Martin and M. P. Heap, "Evaluation of NO_x Emission Characteristics of Alcohol Fuels for Use in Stationary Combustion Systems," presented at the Symposium on Impact of Methanol on Urban Air Pollution, 80th National AIChE Meeting, Boston, Massachusetts, September 7-10, 1975.
17. J. E. Haebig, B. E. Davis, and E. R. Dzuna, "Preliminary Small Scale Combustion Tests of Coal Liquids," presented at ACS Division of Fuel Chemistry, Philadelphia, Pennsylvania, April 1975.
18. M. C. Hardin, "Evaluation of Three Coal Derived Liquid Fuels in A Standard T63 Combustor," Detroit Diesel Allison Report RN 74-28, November 14, 1974.
19. G. B. Martin and E. E. Berkau, "An Investigation of the Conversion of Various Fuel Nitrogen Compounds to Nitrogen Oxides in Oil Combustion," AIChE/Symposium Series Air Pollution and Its Control, Volume 68, 1972.
20. D. W. Turner, R. L. Andrews, and C. W. Siegmund, "Influence of Combustion Modification and Fuel Nitrogen Content on Nitrogen Oxides Emissions from Fuel Oil Combustion," presented at 64th Annual AIChE Meeting, San Francisco, California, November 1971.
21. P. W. Pillsbury, E. N. G. Cleary, P. P. Sigh, and R. M. Chamberlain, "Emission Results from Coal Gas Burning in Gas Turbine Combustors," paper No. 75-GT-44, presented at ASME Gas Turbine Conference, Houston, Texas, March 2-6, 1975.
22. R. D. Klapatch and G. E. Vitti, "Gas Turbine Combustor Test Results and Combined Cycle Systems," Combustion Vol. 45, No. 10, April 1974, pp. 35-38.
23. R. L. Robson and A. J. Giramonti, "The Environmental Impact of Coal-Based Advanced Power Systems," symposium processings; *Environmental Aspects of Fuel Conversion Technology*, EPA-650/2-74-118, NTIS No. PB 238-304/AS, October 1974, pp. 237-257.
24. C. Wilkes and R. H. Johnson, "Effects of Fuel Nitrogen on NO_x Emissions from Gas Turbines," presented at the EPRI NO_x Control Technology Seminar, San Francisco, California, February 5-6, 1976.
25. N. C. Pfefferle, R. V. Carrubba, R. M. Heck, and G. W. Roberts, "Catathermal Combustion: A New Process for Low-Emissions Fuel Conversion," presented at the ASME Winter Meeting, Houston, Texas, November 30 to December 4, 1975.
26. R. V. Carrubba, M. Chang, W. C. Pfefferle, and L. M. Polinski, "Catalytically Supported Thermal Combustion for Emission Control," presented at the EPRI NO_x Control Technology Seminar, San Francisco, California, February 5-6, 1976.
27. T. J. Tyson and J. R. Kliegel, "An Implicit Integration Procedure for Chemical Kinetics," Paper No. 68-180, AIAA 6th Aerospace Sciences Meeting, 1968.
28. V. S. Engleman, "Survey and Evaluation of Kinetic Data on Reactions in Methane/Air Combustion," Exxon Research and Engineering Company, EPA-600/2-76-003, NTIS No. PB 248-139/AS, January 1976.
29. W. Bartok et al., "Laboratory Studies and Mathematical Modeling of NO_x Formation in Combustion Processes," Exxon Research and Engineering Company Final Report No. GRU-3GNOS-71, EPA No. APTD1168, NTIS No. PB 211-480, 1972.
30. A. E. Axworthy, G. R. Schneider, M. D. Schuman, and V. H. Dayan, "Chemistry of Fuel Nitrogen Conversion to Nitrogen Oxides in Combustion," Rocketdyne Division of Rockwell International,

EPA 600/2-76-039, NTIS No. PB250-373/AS, February 1976.

31. E. R. Dzuna, "Combustion Tests of Shale Oils," presented at the meeting of the Central States Section of the Combustion Institute, Columbus, Ohio, April 5-6, 1976.

32. J. S. Ball and H. T. Rall, paper presented at 27th Midyear Meeting of the American Petroleum Institute Division of Refinery, San Francisco, California, 1962.

ENVIRONMENTAL IMPACT AND R&D NEEDS IN COAL CONVERSION*

E. M. Magee, R. R. Bertrand, and C. E. Jahnig†

Abstract

The environmental impact of coal conversion plants is very large. This impact manifests itself in coal and water requirements and solid, liquid, and gaseous emissions. These resource requirements and effluents are discussed for eight gasification and three liquefaction plants. Research and development needs, aimed at minimizing this impact, are also discussed. Special attention is given to areas where sufficient information is lacking for a reliable estimate of the magnitude of the environmental impact.

INTRODUCTION

The impact of coal conversion on the environment can be very large. The magnitude of this impact has been indicated for gasification in references 1 and 2, but the total extent of the impact has not been evaluated because of lack of information concerning many of the factors involved.

Under contract with the Environmental Protection Agency, Exxon Research and Engineering Company has prepared preliminary designs for eleven coal conversion processes, and one chemical coal cleaning process. These processes are listed in table 1. The designs are based on the nonconfidential information available at the time and emphasize the areas of environmental concern.

It is necessary to consider each process when a detailed environmental assessment is to be carried out, but there are certain generalizations that can be made concerning environmental impact of conversion and R&D needs. A paper from this laboratory was presented earlier that dealt with control technology R&D needs (ref. 15). The present paper will emphasize environmental impact and areas where data assessment is needed.

Table 1. Preliminary process designs prepared*

---

o Low- and Medium-Btu Gasification

  - Koppers-Totzek (3)
  - U-Gas (4)
  - Winkler (5)

o High-Btu Gasification

  - BI-GAS (6)
  - HYGAS (7)
  - CO_2 Acceptor (8)
  - Lurgi (9)
  - Synthane (10)

o Liquefaction

  - COED (11)
  - H-Coal (12)
  - SRC (13)

o Chemical Coal Cleaning

  - Meyers (14)

---

*Numbers in parentheses refer to references.

ENVIRONMENTAL IMPACT

The impact of coal conversion manifests itself in resource requirements and in gaseous, liquid and solid effluents. Resource requirements are principally coal and water; there are numerous gaseous, liquid, and solid streams that enter the environment. These process demands on the environment are discussed in this section.

The plants discussed vary in size and no attempt is made to relate the various quantities to products since the purpose is to illustrate the overall environmental requirements. Besides, the various bases differ considerably from process to process. The ranges of the heating value of the products are given in table 2. In this and other tables, approximate values are given for a 100,000 bbl/day petroleum refinery and a 1,000 MWe power plant for comparative purposes.

---

*This work was carried out under contract No. 68-02-0629 with the U.S. Environmental Protection Agency.

†Authors are with the Government Research Laboratories of Exxon Research and Engineering Company, Linden, New Jersey.

Table 2. Heating value of products

Processes	Product Higher Heating Value, 10^6 Btu/hr
Low- and medium-Btu gasification	3,600-10,400
High-Btu gasification	9,800-12,800
Liquefaction	6,900-24,400
100,000 bbl/day refinery (example)	27,000
1,000 MWe power plant (example)	3,400

Raw Water Requirements

Coal conversion plants are large users of raw water, needed for three principal purposes. First, the conversion of coal to liquid or gaseous fuel requires a source of hydrogen since coal is deficient in hydrogen compared to gaseous or liquid hydrocarbons. The only source of this hydrogen is water and this water is chemically converted so that it represents a net water loss. A second water requirement is for quenching and washing various process streams. This water is not destroyed but becomes contaminated with various organic and inorganic chemicals. The third use for water is for cooling process streams. A large fraction of this water is evaporated to provide the cooling effect and this causes a buildup of inorganic salts in the cooling water so that a portion must be purged. Evaporation losses, drift losses and blowdown must be replaced with fresh water.

The ranges of raw water requirements of the processes studied are given in table 3. Also shown for comparison are the requirements for a medium-size petroleum refinery and a large power plant utilizing a recycle cooling system. The largest gasification and liquefaction plants require almost twice as much water as the refinery and about as much as the power plant. These quantities of water are very significant and would place a large environmental burden on many areas where coal is available. Some reduction in water usage is possible with air cooling, but water requirements are still large as some of the process designs include a large fraction of air cooling.

Table 3. Raw water requirements

Processes	Raw Water, gal/min
Low- and medium-Btu gasification	2,400-3,200
High-Btu gasification	2,800-7,100
Liquefaction	3,600-7,600
100,000 bbl/day oil refinery (example)	4,000
1,000 MWe power plant (example)	8,000

Table 4. Energy losses

Processes	Energy Losses, 10^9 Btu/Day
Low- and medium-Btu gasification	50-116
High-Btu gasification	122-154
Liquefaction	118-193
100,000 bbl/day oil refinery (example)	65
1,000 MWe power plant (example)	130

Energy Losses

The next impact to be discussed is net energy consumption of the processes studied. This net energy consumption, or energy "loss," has environmental implications for several reasons. First, it has a direct effect in heat rejected to the surroundings—that is, to air and water. This direct effect may not, however, be as important as the resulting side effects that include the consumption of a proportionate quantity of resources (coal and raw water), the increase in the size of certain plant equipment, and the increased quantities of chemical effluents. Table 4 lists the ranges of the energy losses for the processes studied together with comparative examples for an oil refinery and power plant. The losses for the coal conversion processes are larger than for the oil refinery and the average is about equivalent to that of the power plant. The magnitude of the losses can be better appreciated from the fact that the lost heat is sufficient to provide heating for approximately 100,000 homes.

An approximation of the units responsible for the energy losses is shown in table 5. The assignment of responsibility for the losses shown in table 5 are somewhat subjective—for example, the loss of sensible and latent heat of the main gas stream is assigned to the shift and cooling area. This should, unlike losses due to compression in oxygen production, be prorated over the whole plant. However, no realistic method of such proration is obvious. The sensible heat losses in many minor, miscellaneous streams are assigned rather arbitrarily, but have little effect on the numbers in the table.

The first column of numbers shows losses in the utility and fuel gas sections of the plant. These sections are not themselves part of the gasification scheme; therefore, the losses due to these sections were prorated over those units using fuel gas, electricity, and steam. This proration has a large effect on the gasification section losses because the gasification section is a major user of steam.

The losses due to methanation and pipeline compression, as shown in the table, are distorted due to the fact it was expedient to use extraction turbines in these sections. If the latent heat losses from steam used in steam drives is prorated over all the steam drives, the percentage losses in methanation and pipeline compression become a more realistic 11.9 percent and 6.9 percent respectively. The other numbers in the table would be reduced slightly to make up to 100 percent.

The major revelation from table 5 is that there is no single section of the plant where improvements would have a pronounced effect on the overall thermal efficiency. However, since the total heat losses amount to over 6,000 million Btu/hr, there is room for improvement.

Gaseous Effluents

The major gaseous effluent streams from the processes studied are shown in table 6. These streams are almost as large as the corresponding streams from a large power plant using recycled cooling water. The gaseous effluents from the latter are also shown in the table.

The CO_2 and flue gas streams can contain combustibles, sulfur compounds and oxides of nitrogen. The effluent cooling tower air can contain volatile organic or inorganic compounds that may be present in cooling water from leaks or other sources. The waste nitrogen streams from the oxygen plants are usually clean.

The size of the streams are so large that extreme care must be taken to ensure that they are reasonably clean. Some techniques for controlling pollutants in

Table 5. Thermal losses by unit in Lurgi gasification(1)

Plant Section	Percent of Total Energy Loss	
	Before Proration of Utility and Fuel Gas Losses	After Proration of Utility and Fuel Gas Losses
Coal preparation	0.4	2.2
Oxygen production	13.4	22.6
Gasification and quench	5.7	22.8
Shift and cooling	14.3(2)	14.5(2)
Purification	15.1	18.7
Methanation	6.7	7.7(4)
Pipeline compression	1.1	1.7(4)
Sulfur recovery	1.3	2.4
Gas liquor treating	6.4	7.4
Utilities	17.5(3)	--
Fuel gas production	18.1	--

(1) Based on information from reference 16.

(2) Major losses due to cooling.

(3) Includes miscellaneous areas totaling 0.4%.

(4) Extraction turbines used; if total losses in condensing steam to steam drives is distributed evenly, these numbers become 11.9% for methanation and 6.9% for compression with equivalent reductions in all other areas.

these streams have been discussed earlier in this symposium (ref. 15).

There are other sources of gaseous effluents in coal conversion plants that, though not as large as those shown in the table must, nevertheless, be considered. Such areas as coal storage, evaporation ponds, solids quench, and others must be considered to prevent air pollutants from escaping.

Liquid Effluents

Table 7 lists the ranges of liquid effluents from coal conversion plants, from an example oil refinery and from a large power plant. The numbers listed in the table represent total dirty water except for storm drainage and miscellaneous purges. All of this water may not be discharged as techniques exist for cleaning the water for reuse. The two major sources of dirty water are process

Table 6. Major gaseous effluent streams

Processes	Gaseous effluent streams, ton/day		
	CO_2 + Flue Gas	C.T. Air	Nitrogen
Low- and medium-Btu gasification	4,900-19,200	600,000-2,221,000	0-38,000
High-Btu gasification	45,000-94,000	546,000-3,264,000	0-21,000
Liquefaction	39,000-66,000	1,250,000-2,655,000	6,000-16,000
1,000 MWe power plant (example)	110,000	3,500,000	0

water streams and cooling tower blowdown. The former usually contains organics such as oil, phenols, etc., and inorganics such as ammonia, sulfur compounds, and others. The cooling tower blowdown contains a high concentration of dissolved solids, but may contain organic materials due to leaks.

Also included in table 7, for comparison, are typical dirty water streams for an oil refinery and a large power plant using recycle cooling. As can be seen, the water from coal conversion plants is about equivalent to that from a petroleum refinery and is much greater than that from a power plant. The treatment of these quantities of water for discharge or reuse can be very expensive.

Solid Effluents

Table 8 shows the ranges of solids from coal conversion plants. Also listed is an example quantity of solid waste from a large power plant. Solids from petroleum refineries are relatively modest.

The major solids effluent streams consist of ash from combustion operations and from the gasification or liquefaction steps. The quantities to be disposed of are larger than those from a power plant or from oil refineries. The disposal of these materials may present difficulties.

Impact Summary

The conclusion that can be drawn from this infor-

Table 7. Liquid effluents

Processes	Total Dirty Water,* gal/min
Low- and medium-Btu gasification	600-2,000
High-Btu gasification	1,300-3,500
Liquefaction	1,100-2,400
100,000 bbl/day oil refinery (example)	2,000
1,000 MWe power plant (example)	1,500

*Does not include rain runoff and miscellaneous purges.

Table 8. Solid effluents

Processes	Solids*, ton/day
Low- and medium-Btu gasification	1,000-1,300
High-Btu gasification	1,000-4,900
Liquefaction	700-3,000
1,000 MWe power plant (example)	1,000

*Does not include coal cleaning, flue gas scrubbing, and miscellaneous sludges.

mation is that the impact of a coal conversion plant on the environment is as great as that of a medium-size petroleum refinery or a large coal burning power plant.

R&D NEEDS

The potential, large environmental impact of coal conversion plants requires that effective means be available to control the pollution from exiting streams and to minimize resource requirements. Control technology R&D needs were discussed earlier in this symposium (ref. 15), and the present section of this paper will emphasize data acquisition needs.

Trace Elements

The concentrations of trace elements in coal are fairly well known (refs. 17,18), but far less is known of the disposition of these potentially hazardous chemicals in coal conversion plants. If 20,000 tons/day of coal is used as feed to the plant and this coal contains 1 ppm of a trace element, then 40 pounds/day of that element must appear in streams from the plant.

It is obvious that all materials entering the plant must also leave via the effluent or product streams. Many of the trace elements volatilize to a small or large extent during processing, and many of the volatile components can be highly toxic. This is especially true for mercury, selenium, arsenic, molybdenum, lead, cadmium, beryllium, and fluorine. One study has been made on the trace element content of coal solids after various stages of treatment (ref. 19). A very recent attempt has been made to make a material balance on trace elements in coal gasification (ref. 20). The recovery was variable, ranging from 17 to over 100 percent. Some information is available on the trace element content of liquid products from the SRC process (ref. 13). In general, though, comparatively little information is available as to the eventual fate of the trace elements entering a coal conversion plant and much more data is needed before the potential problem can be evaluated.

R&D Needs in Air Conservation

It will be necessary, of course, to know what elements and compounds are present, and in what quantities, in all gaseous effluent streams. The very magnitude of some of the effluent streams, as shown in table 6, makes the presence of very small traces of pollutants a matter of concern. Other streams, though smaller, may contain larger concentrations of potential pollutants and, therefore, must be controlled.

Table 9 lists some sources of pollutants that could

Table 9. R&D needs in air conservation

- o Determination of quantities of volatiles from cooling towers
- o Quantification of organic losses to air from evaporation ponds and biox units
- o Analysis of combustibles removed with acid gas
- o Control technology where problems exist

very well be overlooked in an investigation of pollution in coal conversion plants.

Cooling water—especially that used against high pressure streams, can pick up trace quantities of volatiles through leaks. These volatiles then enter the atmosphere from cooling towers. Individual petroleum refinery cooling towers in the Los Angeles area were reported to be emitting 3-1,500 pounds of hydrocarbons per day (ref. 21). This source of atmospheric pollution from coal conversion must be evaluated and corrective control procedures taken where necessary.

Evaporation ponds and biological oxidation (biox) units can be sources of atmospheric pollution. Several papers have pointed out the increase in microbial concentrations in the air near sewage treatment plants (refs. 22,24). Thibodeaux and Parker (ref. 25) have developed equations for calculating the concentration of volatiles in the air near aerated basins. Techniques for handling dirty water, such as evaporation ponds and biox units, can—unless care is taken—transfer a water pollution problem into an air pollution problem. If this happens, more R&D is necessary to produce technology to allow water treatment without air contamination.

Another area deserving attention is the removal of combustibles along with acid gas from coal conversion streams. This possibility is recognized for absorption systems and means to control the effluent of the combustibles have been indicated in one case (ref. 16). Other systems such as hot potassium carbonate also absorb gases such as hydrogen, carbon monoxide,and methane (ref. 26). A better definition of potential problems that may result in coal conversion plants is needed.

When these problems in the area of air conservation are better defined, appropriate R&D is needed to produce technology to solve the problems.

R&D Needs in Water Conservation

Table 10 lists some specific areas for data acquisition needed in the area of water pollution control in coal conversion plants. One item needed is a better water analysis than is presently available where materials are lumped as oxygen demand. Since many compounds—such as certain aromatics—are not readily biodegradable, their presence in water effluents does not show up as biological oxygen demand. Analysis for specific chemicals in effluent water is needed together with a determination of their fate in conventional wastewater treatment facilities.

Another area for R&D is an effort to determine quantities of miscellaneous purge streams and their compositions. For example, published information on the solution purge from Stretford units used in desulfurizing coke oven gas indicates a large variation in the quantities of purge (ref. 27). A better definition of such streams in coal conversion plants will indicate what further R&D is necessary to minimize the environmental impact of such streams.

Table 10. R&D needs in water conservation

- Analysis for specific constituents in dirty process water
- Documentation of quantities and qualities of miscellaneous purge streams (e.g., from acid gas removal)
- Analysis of leachate from coal storage, ash, other solids
- Control technology where problems exist

An examination of the leachability of inorganic materials from coal, ash, and other solids from coal conversion plants is needed. The ash from liquefaction units and gasifiers will probably differ from the ash from coal combustion. The knowledge as to whether water runoff or seepage from such solids is innocuous would be of value.

Control technology necessary to remove any environmental danger from water pollution must await further problem definition in the area.

Data Acquisition in Coal Conversion Plants

An analytical test plan has been formulated to facilitate data acquisition in coal conversion plants. Using an example coal gasification plant and a coal liquefaction plant, a detailed list of streams where analyses might be required was made (ref. 28). Table 11 shows a summary of the streams.

Twenty streams in gasification and 23 in liquefaction are the minimum that would have to be sampled and analyzed to make a pollutant material balance. If a balance could not be obtained due to errors or other causes, it might be necessary to sample and analyze as many as 29 other streams in gasification and 38 in liquefaction in order to determine the cause of the imbalance. The example gasification plant has 72 streams and the example liquefaction plant has 75 streams. For various reasons, it is conceivable that all these streams would have to be sampled and analyzed.

The magnitude of the problem is increased by the number of analyses that may be required for each stream. The Analytical Test Plan gives the method for

Table 11. Stream analysis requirements for typical conversion plants

	Gasification	Liquefaction
Minimum streams to be analyzed for pollutant material balance	20	23
Additional stream analyses to determine errors	28-29	37-38
Total streams identified where analyses may be required	72	75

those analyses shown in table 12. Of course, not all the analysis would have to be carried out for each sample, but the magnitude of the effort required is truly large.

CONCLUSIONS

The potential impact of coal conversion plants on the environment is large. The magnitude of the impact is comparable to that of a medium-size petroleum refinery or a large coal-burning power plant. When it is realized that the impact of coal conversion is an additional impact—that is, it does not replace refining or ultimate fuel utilization—the drive to minimize the effects of coal conversion becomes even more significant.

The large size of the potential environmental implications of coal conversion requires a comparable amount of new information and technology needs. The R&D effort needed to assure that coal conversion can be carried out in an environmentally sound way is indeed also very large.

Table 12. Analyses to be performed

Material	Number of Analyses
Metals	17
Gases	16
Polynuclear aromatics	14
Other organic materials	9
Inorganic ions	7
Coal, ash and char	11
Water quality indicators	12
Particulates	--

REFERENCES

1. W. J. Rhodes, "Environmental Impact of Coal Gasification," in "Air: I. Pollution Control and Clean Energy," C. Rai and L. A. Spielman, Eds., AIChE Symposium Series 147, Vol. 71, 1975, pp. 154-159.
2. C. E. Jahnig and R. R. Bertrand, "Environmental Aspects of Coal Gasification," presented at the AIChE Meeting, Boston, Mass., Sept. 1975.
3. E. M. Magee, C. E. Jahnig, and H. Shaw, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification; Section 1: Koppers-Totzek Process," EPA-650/2-74-009a, January, 1974. NTIS PB-231 675.
4. C. E. Jahnig, "ibid Section 7: U-Gas Process," EPA-650/2-74-009i, August 1975.
5. C. E. Jahnig, "ibid Section 8: Winkler Process," EPA-650/2-74-009j, September 1975.
6. C. E. Jahnig, "ibid Section 5: BI-GAS Process," EPA-650/2-74-009g, May 1975. NTIS PB-243 694.
7. C. E. Jahnig, "ibid Section 6: HYGAS Process," EPA-650/2-74-009h, August 1975.

8. C. E. Jahnig and E. M. Magee, "ibid Gasification; Section 4: CO_2 Acceptor Process," EPA-650/2-74-009d, December 1974. NTIS PB-241 141.
9. H. Shaw and E. M. Magee, "ibid Section 3: Lurgi Process," EPA-650/2-74-009c, July 1974. NTIS PB-237 694.
10. C. D. Kalfadelis and E. M. Magee, "ibid Section 2: Synthane Process," EPA-650/2-74-009b, June 1974. NTIS PB-237 113.
11. C. D. Kalfadelis and E. M. Magee, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Liquefaction; Section 1: COED Process," EPA-650/2-74-009e, January 1975. NTIS PB-240 372.
12. C. E. Jahnig, "ibid Section 3: H-Coal Process," EPA-650/2-74-009m, October 1975.
13. C. E. Jahnig, "ibid Section 2: SRC Process," EPA-650/2-74-009f, March 1975. NTIS PB-241 792.
14. E. M. Magee, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Coal Treatment; Section 1: Meyers Process," EPA-650/2-74-009k, September 1975.
15. C. E. Jahnig, R. R. Bertrand and E. M. Magee, "Environmental Impact and R&D Needs in Coal Conversion," this symposium.
16. Anon, "El Paso Natural Gas Company Burnham Coal Gasification Complex-Plant Description and Cost Estimate," prepared by Stearns-Roger, Inc., August 16, 1972 (Rev. 9/20/72). Application of El Paso Natural Gas Company before U. S. Power Commissions, Docket No. CP 73-131, November 15, 1972 (Rev. Oct. 1973).
17. E. M. Magee, H. J. Hall and G. M. Varga, Jr., "Potential Pollutants in Fossil Fuels," EPA-R2-73-249, June 1975. NTIS PB-225 039.
18. H. J. Hall, G. M. Varga, Jr. and E. M. Magee, "Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology," St. Louis, Missouri, May 1974, EPA-650/2-74-118, pp. 35-47.
19. A. Attari, "The Fate of Trace Constituents of Coal During Gasification," EPA-650/2-73-004, August 1973.
20. A. J. Forney et al., "Trace Element and Major Component Balances Around the Synthane PDU Gasifier," Pittsburgh Energy Research Center, Report No. PERC/TPR-75/1, August 1975.
21. U.S. Department of Health, Education, and Welfare, "Atmospheric Emissions from Petroleum Refineries," PHS NO. 763, 1960. NTIS PB-198 096.
22. P. J. Napolitano and D. R. Rowe, *Water and Sewage Works*, *113*, Dec. 1966, p. 480.
23. A. P. Adams and J. C. Spendlowe, *Science*, *169*, Sept. 1970, p. 1218.
24 L. J. Thibodeaux and N. J. Carter, "Recent Advances in Air Pollution Control," AIChE Symposium Series, Vol. 70, No. 137, AIChE, New York, 1974.
25 L J. Thibodeaux and D. G. Parker, "Desorption Limits of Selected Industrial Gases and Liquids from Aerated Basins," Paper No. 30D, AIChE Meeting, Tulsa, March 1974.
26. J. H. Field et al., "Pilot Plant Studies of the Hot-Carbonate Process for Removing Carbon Dioxide and Hydrogen Sulfide," Bureau of Mines Bulletin 597, U.S. Gov't Printing Off., 1962.
27. A. J. Moyes and J. S. Wilkinson, *The Chemical Engineer*, Feb. 1974, p. 84.
28. C. D. Kalfadelis et al., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Analytical Test Plan," EPA-650/2-74-009-1, October 1975.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. **EPA-600/2-76-149**

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE **Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, II (December 1975, Hollywood, Florida)**

5. REPORT DATE **June 1976**

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) **Franklin A. Ayer (Compiler)**

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Research Triangle Institute
P.O. Box 12194
Research Triangle Park, North Carolina 27709

10. PROGRAM ELEMENT NO. **EHB529**

11. CONTRACT/GRANT NO. **68-02-1325, Task 57**

12. SPONSORING AGENCY NAME AND ADDRESS

EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED **Final; 2-4/76**

14. SPONSORING AGENCY CODE **EPA-ORD**

15. SUPPLEMENTARY NOTES **IERL-RTP Task Officer for this report is William J. Rhodes, Mail Drop 61, Ext 2851.**

16. ABSTRACT

The report covers EPA's second symposium on the environmental aspects of fuel conversion technology. The symposium was conducted at the Diplomat Hotel, Hollywood, Florida, December 15-18, 1975. Its main objective was to review and discuss environmentally related information in the field of fuel conversion technology. Specific topics were environmental problem definition, process technology, control technology, and process measurements.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Process Variables	Air Pollution Control	13B	13H,07A
Fuels	Industrial Processes	Stationary Sources	21D	
Conversion	Control	Problem Definition		
Environmental	Measurement	Process Technology		14B
Engineering		Control Technology	05E	
Environments		Process Measurements		

18. DISTRIBUTION STATEMENT **Unlimited**

19. SECURITY CLASS *(This Report)* **Unclassified**

20. SECURITY CLASS *(This page)* **Unclassified**

21. NO. OF PAGES

22. PRICE

EPA Form 2220-1 (9-73)

*U.S. GOVERNMENT PRINTING OFFICE: 1976-641-317/5515 Region No. 4